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Structure and Proton-Donating Ability of Trifluoro-*N*-(2-phenylacetyl)methanesulfonamide

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Abstract—According to the data of quantum-chemical calculations and IR spectroscopy the trifluoro-N-(2-phenylacetyl)methanesulfonamide $CF_3SO_2NHC(O)CH_2Ph$ in the isolated state and in inert media exists in the form of two conformers with the syn- and antiperiplanar orientation of the C=O and N–H bonds. Its self-associates in the CCl_4 solution and in molecular crystals constitute cyclic dimers formed by the NH···O=S bonds and chain dimers with the NH···O=C bonds. As a hydrogen bond donor, trifluoro-*N*-(2-phenylacetyl)methanesulfonamide is stronger than *N*-methyltrifluoromethanesulfonamide. Its pK_a in methanol is 5.45, that is 5 pK units lower than for amides CF_3SO_2NHR and 2 pK units higher than for imide $(CF_3SO_2)_2NH$.

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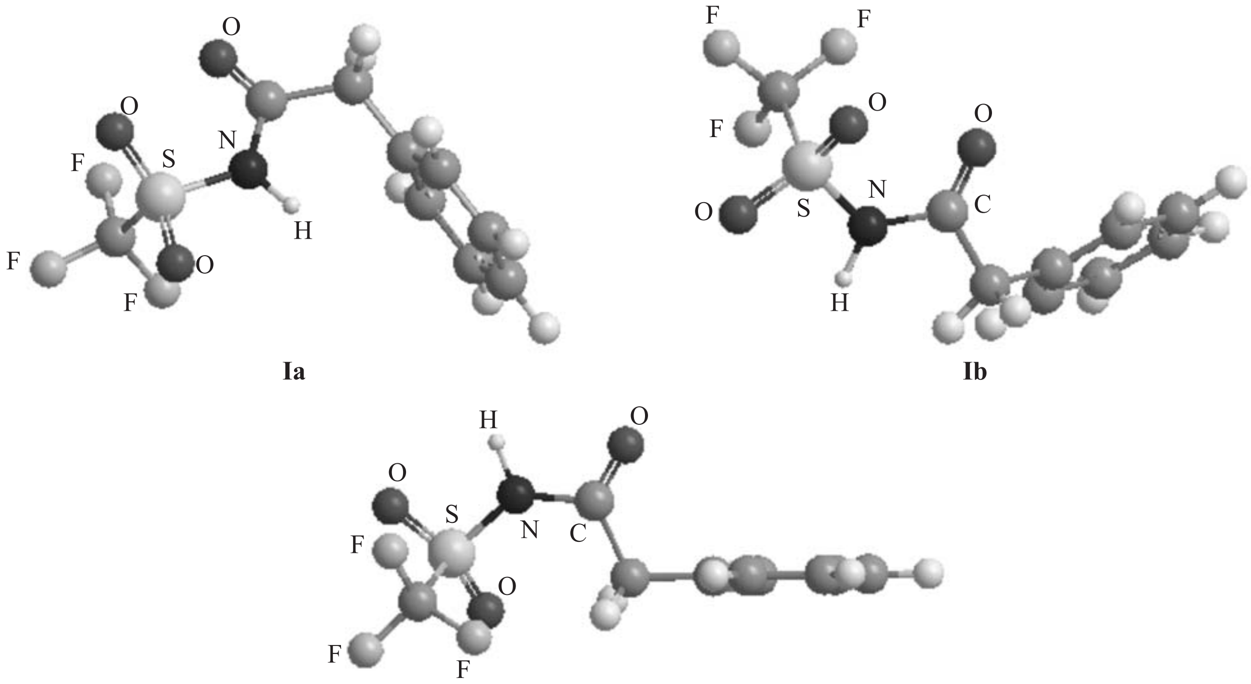
N-Acylperfluoroalkanesulfonamides $R_FSO_2NHC\cdot(O)R$ are mixed imides of carboxylic and perfluoroalkanesulfonic acids. The presence of two electron-withdrawing groups at nitrogen atom in their molecules should result in high NH-acidity of these compounds. This, in conjunction with the presence of the two centers of basicity, may provide formation of supramolecular aggregates of various structure not only in the crystal but also in solutions and even in the gas phase. Such a conclusion originates from the results of our previous studies according to which even less acidic amides CF_3SO_2NHR (R = H, Me) are strong NH-acids that form stable self-associates surviving in the gas phase at high temperatures (>400 K) [1, 2]. In the crystal, trifluoromethanesulfonamide $CF_3SO_2NH_2$ as well as methanesulfonamide $CH_3SO_2NH_2$ form cyclic dimers which are linked into infinite bands by intermolecular hydrogen bonds N–H···O=S [1, 3]. In the crystal, more acidic imides of sulfonic $(RSO_2)_2NH$ and carboxylic acids $(RCO)_2NH$ form supramolecular aggregates whose structure depends on the substituents at the nitrogen atom. Thus, bis(trifluoromethanesulfonyl)imide $(CF_3SO_2)_2NH$ constitutes a supramolecular structure formed by relatively weak hydrogen bonds with participation of both oxygen atoms from one molecule [4]. At the same time, bis(phenylsulfonyl)imide $(PhSO_2)_2NH$ in the crystal forms chains with strong H-bonds involving one oxygen atom of the adjacent molecule [5] whereas bis(ethylsulfonyl)imide $(EtSO_2)_2NH$ forms dimers by means of two linear H-bridges [6]. Fluorine-containing imides of carboxylic acids, the imide of trifluoroacetic acid $(CF_3CO)_2NH$ and acetyltrifluoroacetamide $CF_3C(O)\cdot NH(CO)CH_3$, form in the crystal bifurcated hydrogen bonds [7]. From the X-ray diffraction data, nonvalent distances NH···O in the above dimers vary in a large range although for the H-bonds of different types these variations cannot be unambiguously correlated with variation in their strength. In solutions, when the formation of homo- and heteroassociates is possible, the supramolecular structure is determined both by the properties of the dissolved NH-acid and the nature of the solvent.

Trifluoro-*N*-(2-phenylacetyl)methanesulfonamide $CF_3SO_2NHC(O)CH_2Ph$ **I** we recently prepared along with other *N*-acyltrifluoromethanesulfonamides $CF_3SO_2\cdot NHC(O)R$ by the reaction of *N*-sulfinyltrifluoromethanesulfonamide CF_3SO_2NSO with carboxylic acids RCOOH [8]. It contains two different basic centers, the carbonyl and the sulfonyl groups. Due to this fact, its self-associates can form chains by means of bifurcate hydrogen bonds involving the oxygen atoms of the carbonyl and the sulfonyl groups as well as cyclic or chain dimers with the NH···O=C or NH···O=S bonds. In the present work, the structure of compound **I** in the isolated and crystal state and in inert media as well as the structure of its dimers **II** and model dimers **III** was studied using the methods of IR spectroscopy and quantum-chemical calculations at the B3LYP/6-311G** level. The proton-donating ability of compound **I** in the interaction with the Lewis bases was quantitatively estimated and the pK_a value in methanol was measured.

The value of pK_a for imide **I** measured by the method of potentiometric titration in methanol is equal to 5.45, which is indicative of a high acidity of compound **I** caused by the presence of two electron-withdrawing groups at the nitrogen atom. As compared with amides CF_3SO_2NHR (R = H, CH_3, $CH_2NH\cdot SO_2CF_3$, $CH_2NHCOCH_3$) for which the values of pK_a measured in the same solvent fall in the range of 10.1–12.7 pK units [9], imide **I** is more acidic by ~5 orders of magnitude. However, since the RC(O) group is a weaker acceptor than RSO_2 {$\sigma_n(CH_3CO)$ 0.50, σ_n (CF_3SO_2 0.93) [10]}, imide **I** is by ~2 pK units less acidic than bis(trifluoromethanesulfonyl)imide $(CF_3SO_2)_2\cdot NH$ for which the value of pK_a also measured in methanol is 2.7 [11]. Earlier, the conclusion was made that the acidity of *N*-substituted trifluoromethanesulfonamides was determined not only by electron-withdrawing properties of the substituent at the nitrogen atom but also by nonvalent interactions in their molecules, which governed the character of the associates formed in solutions [9].

Quantum-chemical calculations of the isolated molecule of imide **I** revealed the presence of three conformers corresponding to the minima on its potential energy surface (Fig. 1, Table 1). The most stable is conformer **Ia** with the *anti*-periplanar *ap*-orientation of the amide group and the *syn*-periplanar *sp*-orientation of the O=S–N–H fragment for one of oxygen atoms of the sulfonyl group. The NH group proton in conformer **Ia** is located above the plane of the benzene ring approximately in the direction of the π-orbital of the *ipso*-carbon atom with the internuclear distance $d(NH\cdots C_{ipso})$ 2.395 Å, which is 0.5 Å less than the sum of the van der Waals radii of the C and H atoms. This suggests the presence of an intramolecular hydrogen bond of the NH···π-type in conformer **Ia** that is responsible for its highest stability. Large dipole moment of conformer **Ia** (5.71 D) accounts for its preferable stabilization also upon an increase in the polarity of the medium. Conformer **Ib** formed from conformer **Ia** by rotation by 180° around the CH_2–C(O) bond by 1.91 kcal mol^{-1} less stable than conformer **Ia**



Ia

Ib

Ic

Fig. 1. Molecular structure of the conformers of trifluoro-*N*-(2-phenylacetyl)methanesulfonamide **I**.

and is also characterized by a high dipole moment (4.75 D). The energy of conformer **Ic** with the *sp*-orientation of the amide group is only 0.19 kcal mol^{-1} higher than that of conformer **Ia** but its dipole moment is substantially less, 2.14 D. It is worth mentioning that rotamers of structures **Ia** and **Ic** about the S–N bond with the dihedral angles OSNH of ~30° do not correspond to minima on the potential energy surface and during optimization are transformed into the structures with the *sp*-arrangement of the OSNH group and a shortened contact between the oxygen and hydrogen atoms (2.5 Å). Note also that structures **Ia–Ic** cannot be interconverted due to the restricted rotation about the N–C bond in amides. Quantum-chemical calculations predict an eclipsed orientation of the SO_2 group with respect to the NH_2 group also in sulfonamide HSO_2NH_2 caused by the repulsion between the lone electron pairs of the nitrogen and oxygen atoms in the restricted conformation [12]. By the data of electron diffraction and quantum chemical calculations, the eclipsed orientation of the S=O and N–H bonds is preferable also for benzenesulfonamide (by 0.7–1.1 kcal mol^{-1} depending on the method of calculation) [13] and is stabilized, as presumed by Petrov et al., by the intramolecular hydrogen bond NH···O=S.

The factors determining the stability of different conformers of bisimides are steric effects, dipole-dipole interactions between the polar groups, hydrogen bonds of different types, as well as the crystal packing effects [14]. Thus, the crystalline imide of propionic acid $(PrCO)_2NH$ exists as the conformer with the *ap*,*ap*-orientation of the N–H and C=O groups due to, as believe Nandini et al., the packing effects and the formation of bifurcated hydrogen bonds, although for the isolated molecule in the gas phase and in solutions the calculations predict the predominance of the more stable *sp*,*ap*-conformer [14]. For the heterocyclic derivative of trifluoromethanesulfonamide, 3,5-bis(trifluoromethylsulfonyl)-1,3,5-oxadiazinane, it was shown experimentally by the XRD method that due to the packing effects in the crystal that conformer is “frozen out” which in the solution, by the NMR data, is the minor one [15].

Close values of the energies of the conformers of compound **I** having substantially different dipole moments result in the dependence of their relative population on the polarity of the medium and the nature of the formed intermolecular hydrogen bonds.

Table 1. Calculated energy differences ΔE, dipole moments μ, frequencies ν(NH) of conformers of compound **I**, its dimers **II**, and model dimers **III**, energies of formation of H-bonds in dimers ΔE_H, internuclear distances d(H···O), differences of vibration frequencies of the free and associated NH groups $\Delta\nu$(NH)

Comp. no.	ΔE, kcal mol^{-1}	μ, D	$-\Delta E_H$, kcal mol^{-1a}	d(H···O), Å	ν(NH), cm^{-1}	$\Delta\nu$(NH), cm^{-1}
Ia	0	5.71			3550	
Ib	1.91	4.75			3593	
Ic	0.19	2.14			3551	
IIa	0	3.38	16.67 (8.34)	1.852 1.862		
IIb	0.14	3.16	13.09 (6.54)	1.824		
IIc	1.47	6.74	13.29	1.844		
IId	4.15	1.45	9.08 (4.54)	1.939		
IIIa	2.98	1.82	14.93 (7.46)	1.844	3380	207
IIIb	0	3.05	13.40 (6.70)	1.814	3239	315
IIIc	6.67	5.90	11.24	1.856	3364	223
IIId	4.21	1.88	9.19 (4.60)	1.938	3415	139

[a] In parentheses are given the values calculated per one H-bond.

The IR spectrum of a diluted solution of compound **I** in CCl_4 (C ~10^{-4} M) contains a high-frequency doublet band ν(NH) with the more intense component at 3363 cm^{-1} and the less intense one at 3323 cm^{-1} (Fig. 2a, Table 2). The ratio of intensity of the components does not vary with concentration of the solution in the range of 10^{-3}–10^{-5} M which points to the fact that they belong to free NH groups of the monomer molecules of compound **I** in two different forms. A decrease in the temperature of the solution to –20°C does not lead to redistribution of their intensity, either. At the same time, a decrease in the temperature of the solution of compound **I** in polar CH_2Cl_2 leads to variation of the frequency and the shape of the bands. At 25°C, the more intense high-frequency component of the ν(NH) band suffers a low-frequency shift relative to the spectrum of the solution in CCl_4 to 3331 cm^{-1}, as does its shoulder (3311cm^{-1}). At –80°C the observed band becomes a singlet with the maximum shifted to low frequencies by 18 cm^{-1} as compared to that at room temperature. This suggests that the conformers ratio is changed in favor of the more stable one corresponding to the low-frequency

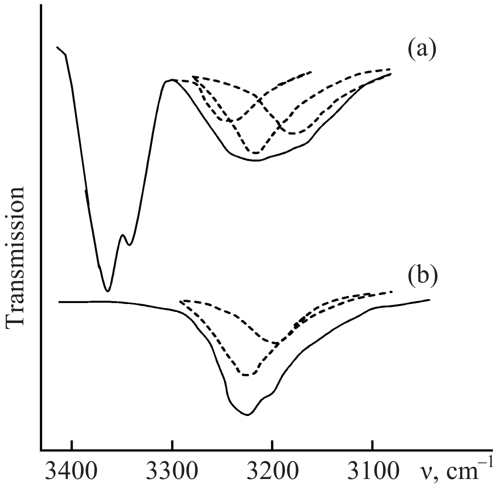


Fig. 2. IR spectra in the ν(NH) region of trifluoro-*N*-(2-phenylacetyl)methanesulfonamide: (a) in CCl_4 solution (c ~10^{-3} M) and (b) in KBr.

component. The ν(C=O) band characterizing the monomer molecules of compound **I** in its spectrum in CCl_4 solution (c ~10^{-4} M) is located at 1762 cm^{-1}. In more polar solvent CH_2Cl_2 it remains practically at the same wavenumber (1758 cm^{-1}).

A wide band ν(NH) in the spectrum of the solution of compound **I** in CCl_4 corresponding to its NH groups involved in the formation of self-associates has three poorly resolved maxima. Therefore, we performed separation of the general band contour to three Lorentz components with the maxima at 3227, 3215, and 3177 cm^{-1} (Fig. 2a). With dilution, the intensity of this band decreases to complete disappearance at c ~10^{-5} M.

The IR spectrum of compound **I** in the crystalline state (Fig. 2b) is characterized by a weak band of stretching vibrations of the associated NH groups at 3225 cm^{-1} having a shoulder at the low-frequency wing (3194 cm^{-1}). This band correlates with the intense band of stretching vibrations of the associated C=O groups at 1729 cm^{-1}. Close values of ν(NH) of the maxima of the bands of the associated NH groups in the spectra of compound **I** in the solid state and in CCl_4 suggest that its molecules form dimers of a similar type in the crystal and in an inert solvent.

Earlier it was shown that the calculated absolute values of the ν(NH) vibration frequencies for trifluoromethanesulfonamide, its derivatives and their associates are substantially higher than those observed experimentally. Nevertheless, the difference between these values, Δν(NH), when several NH groups are present in the molecules and their associates, or between the values of ν(NH) of the molecules and their associates is in good agreement with the data of IR spectroscopy [1, 2, 16]. The frequency difference between the maxima of the doublet band of the free NH group vibrations in the spectrum of the solution of compound **I** in CCl_4 is 40 cm^{-1}. It corresponds to that for the values of ν(NH) in the calculated vibration spectra of conformers **Ia, Ic** having the same frequency 3550 cm^{-1} and conformer **Ib** (3593 cm^{-1}) (Table 1). Based on the absence of the temperature dependence between the components of the doublet band ν(NH) in the spectrum of solution of compound **I** in CCl_4, it may be concluded that they characterize forms **Ib, Ic**. In polar CH_2Cl_2 there is a dynamic equilibrium between the conformers **Ib** and **Ia**. The

Table 2. Frequencies of stretching vibrations of N–H bonds, ν(NH) and difference between the values of ν(NH) for free NH groups and those associated with Lewis base, Δν(NH) (cm^{-1})

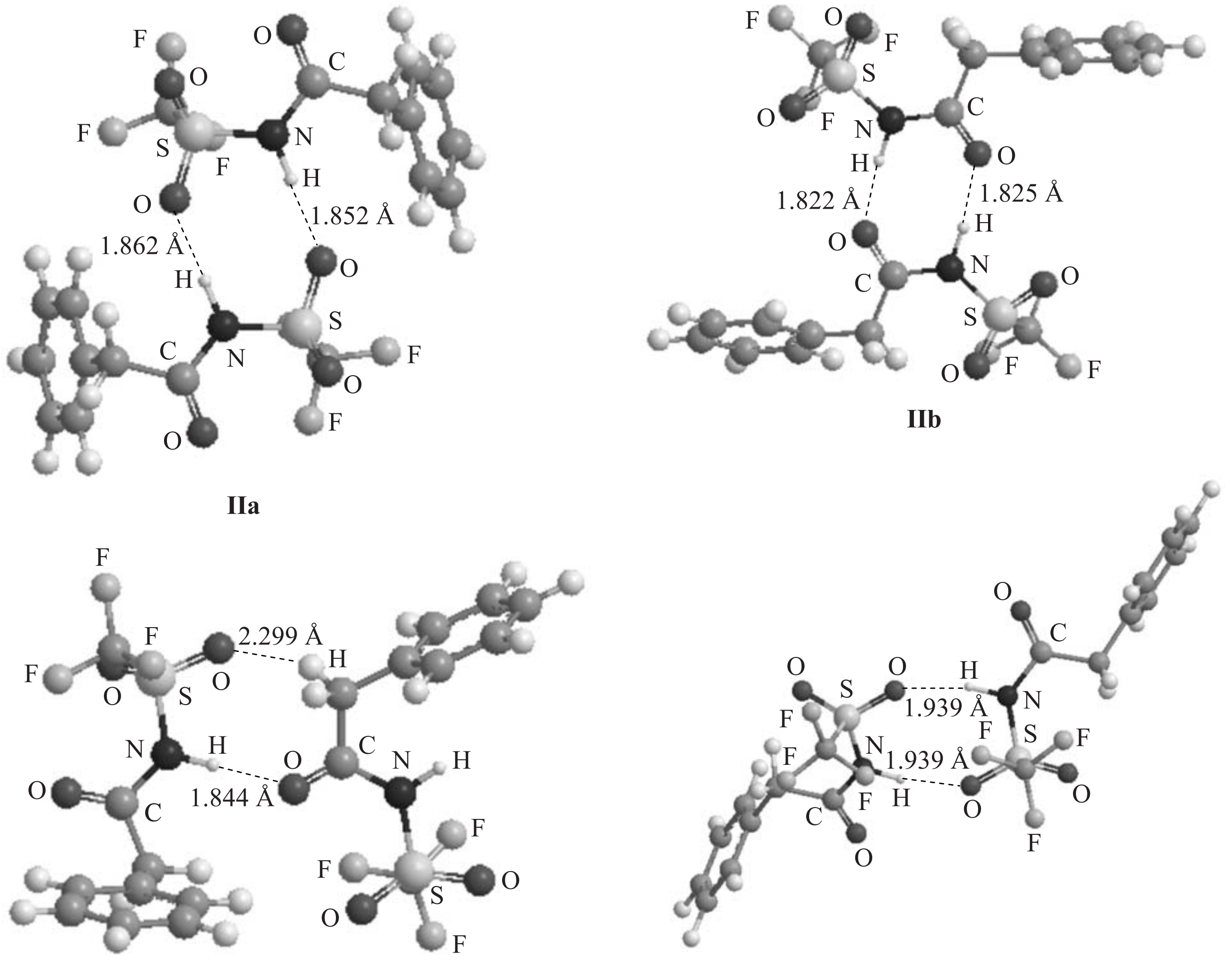
Comp. no.	ν(NH), cm^{-1}		Δν(NH), cm^{-1}				
	CCl_4	KBr	Solution in CCl_4			B3LYP/6-311G**	
			DMF	Dioxane	Acetonitrile	Dioxane	Acetonitrile
I	3363 s 3323 m 3227 m 3215 sh 3177 sh	3225 w 3194 sh	>300	>300	186	364	202
IV	3407 3316	3300[a]	272	243	137	255	154

[a] In thin layer.

decrease of the temperature of the solution is followed by a shift of this equilibrium toward the more stable conformer **Ia**.

A wide band of the associated NH groups in the spectrum of the solution of compound **I** in CCl_4 (Fig. 2a) corresponds to the formation in an inert medium of its self-associates of three types, at least two of which exist also in the molecular crystal. The shift of its maxima Δν(NH) from the high-frequency component of the free NH group band is 136, 148, and 186 cm^{-1}, and from the low-frequency component, 96, 108, and 146 cm^{-1}. In order to identify the type of H-bonding in the self-associates formed we have performed geometry optimization and energy calculation of the possible dimer structures **IIa–IId** (Fig. 3, Table 1). Because of complex structure of dimers **IIa–IId** the calculation of frequencies of normal vibrations was performed for model dimers **IIIa–IIId** in which the benzyl group was replaced by a methyl group (Table 1).

The most stable is cyclic dimer **IIa** formed from conformers **Ia** by closure of two intermolecular hydrogen bonds NH···O=S. During the geometry optimization the intramolecular hydrogen bond NH···π in components **Ia** is broken and they are converted into form **Ib**. Dimer **IIa** has symmetry close to C_2 with the axis of symmetry passing through the center of the chelate cycle perpendicular to it (Fig. 3). Nonvalent distances NH···O in dimer **IIa** are by 0.014–0.024 Å longer than in the analogous cyclic dimer of imide $(CF_3SO_2)_2NH$ and 0.026–0.036 Å shorter than in the similar cyclic dimer of amide CF_3SO_2NHMe, in accordance to the order of their relative acidity [9, 11]. The chain dimer with the NH···O=S bond was also optimized into the cyclic dimer **IIa**. The cyclic dimer **IIb** closed by two intermolecular hydrogen bonds NH···O=C with participation of the *sp*-oriented amide groups and also having C_2 symmetry is only by 0.14 kcal mol^{-1} less stable than dimer **IIa**. The chain dimer **IIc** with short intermolecular hydrogen bond



IIa **IIb**

IIc **IId**

Fig. 3. Molecular structure of dimers of trifluoro-*N*-(2-phenylacetyl)methanesulfonamide.

NH···O=C of 1.844 Å and shortened contact CH···O=S of 2.3 Å is by 1.47 kcal mol^{-1} less stable than **IIa**. Its component acting as a donor of intermolecular hydrogen bond NH···O=C has the conformation of dimer **Ib** whereas in the second component retaining the conformation of dimer **Ia**, the hydrogen bond NH···π becomes shorter by 0.03 Å. However, the energy of formation of one H-bond NH···O=S (ΔE_H) in the cyclic dimer **IIa** calculated as the difference between the total energy of the H-complex and the sum of the energies of its components is ~2 kcal mol^{-1} larger than that of one H-bond NH···O=C of the cyclic dimer **IIb** in which the internuclear distance H···O is shorter by 0.03 Å.

Replacement of the benzyl group in dimers **IIa–IId** by methyl reduces steric hindrances and the order of the energetic stability of model dimers **IIIa–IIId** differs from that for **IIa–IId** (Table 1). The most stable becomes the cyclic dimer **IIIb** with the shortest H-bonds NH···O=C of 1.814 Å. The energy of their formation slightly differs from those in analogous dimer **IIb**. Cyclic dimers **IIIa** and **IIId** with the NH···O=S bonds and chain dimer **IIIc** with the NH···O=C bond by the length of the intermolecular hydrogen bonds and the energy of their formation are also close to the corresponding dimers **IIa,IIc**, and **IId**. From this follows the validity of assigning the structure of dimers **IIa–IId** by comparing the values of ν(NH) calculated for the model dimers **IIIa–IIId** with the experimentally measured figures for compound **I**. The calculated value of the vibration frequency for the associated NH groups of dimer **IIIb** shows the largest shift with respect to ν(NH) of its components [Δν(NH) 315 cm^{-1}]. The chain dimer **IIIc** is characterized by a smaller shift Δν(NH) of 223 cm^{-1}. This is consistent with the larger length of the NH···O=C bond in dimer **IIIc** than in cyclic dimer **IIIb** by 0.042 Å although the energy of formation of this bond in dimer **IIIc** is by 4.5 kcal mol^{-1} higher than for one NH···O=C bond in dimer **IIIb**. The shift of the same order Δν(NH) 207 cm^{-1} takes place in dimer **IIIa** with the NH···O=S bonds. Cyclic dimer **IIId** formed from two conformers **Ic** with the *sp*-orientation of the amide group by the closure of two intermolecular hydrogen bonds NH···O=S has C_2 symmetry and is characterized by the lowest energy of formation of these bonds of 4.6 kcal mol^{-1}, their maximum length of 1.938 Å, and the lowest Δν(NH) value of 139 cm^{-1}. The values of Δν(NH) for dimers **IIIa** and **IIIc** are close to each other and by almost 100 cm^{-1} lower than those in the cyclic dimer **IIIb**. The shifts Δν(NH) determined from the spectrum of the solution of compound **I** in CCl_4 as the differences between the three maxima of the band of the associated NH groups and two maxima of the band of the free NH groups lie in the interval of 100–200 cm^{-1}. They correspond to the values of Δν(NH) calculated for the NH···O=S bonds in the cyclic dimers **IIIa** and **IIId** and for the NH···O=C bond in the chain dimer **IIIc**.

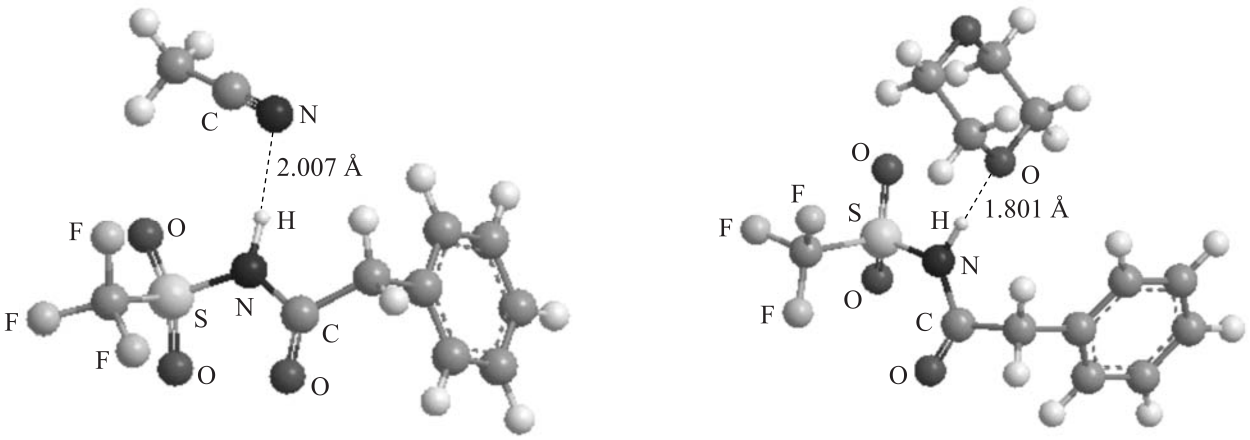
A close analog of compound **I** is the molecule of *o*-sulfobenzimide (saccharin) with the *sp,sp*-orientation of the sulfonyl and carbonyl groups with respect to the N–H bond. According to the X-ray diffraction data, its molecules in the crystal represent cyclic dimers formed by two bridge bonds NH···O=C [17]. The vibration band of the associated C=O groups of this compound is located at 1721 cm^{-1} (KBr) and that of the free C=O groups at 1733 cm^{-1} (DMSO) [18]. With this, the vibration band of the associated NH groups in the IR spectrum of its molecular crystal lies at 3100 cm^{-1} being shifted by 300 cm^{-1} to low frequencies relative to the spectrum of its solution in CCl_4 [19], which is close to the calculated value of Δν(NH) for the cyclic dimer **IIIb** with the NH···O=C bonds. Chain dimers with the NH···O=C bonds are formed in the molecular crystal of 2-cyano-4-phenylglutarimide [20] also having the *sp,sp*-orientation of the carbonyl groups with respect to the N–H bond. They are characterized by the band ν(NH) at 3294 cm^{-1}. Its frequency is by 194 cm^{-1} higher than that of the cyclic dimers of saccharin, which is qualitatively consistent with the larger value of ν(NH) for the chain dimer **IIIc** than for its cyclic analog **IIIb** by 125 cm^{-1}.

Therefore, compound **I** in the CCl_4 solution and in the crystalline state exists in the form of cyclic dimers **IIa** with the NH···O=S bonds and chain dimers with the NH···O=C bonds. In compliance with the low value of ν(C=O) of 1730 cm^{-1} in the spectrum of the solid compound its molecular crystal is predominantly formed by the latter. Formation of the chain dimer **IIc** rather than the energetically preferable cyclic dimer **IIb** may be due to the increase of the dipole moment as compared to that of the monomeric components upon association of the former and its decrease upon association of the latter (Table 1). In a condensed medium the forms with higher dipole moment become preferable.

One of the main factors determining the type of the hydrogen bond in the associates of compound **I**

(NH···O=S or NH···O=C) is the relative spectroscopic basicity of the carbonyl and the sulfonyl group in its molecule. It is known from the literature that the proton affinity (PA) or thermodynamic basicity of the C=O group is lower than that of the S=O group in sulfoxides but higher than that of the S=O group in sulfones [21]. This is true both for carboxamides and sulfonamides. Thus, the values of PA calculated using the MP2 method with various basis sets for molecules $HCONH_2$ and $MeSO_2NH_2$ are 209.5 and 201.9 kcal mol^{-1} (although the experimental value of PA for formamide is substantially lower, 198.4 kcal mol^{-1} [21]). Spectroscopic basicity may have no correlation with the thermodynamic basicity, therefore, to estimate the affinity of the C=O and S=O groups in the molecule of compound **I** to the hydrogen bond donors we have calculated the isomeric H-complexes of molecule **I** with methanol coordinated to the C=O or S=O group. H-Complex with the MeOH···O=C bond turned out to be 3.4 kcal mol^{-1} more stable than that with the MeOH···O=S bond, and the shift of the ν(OH) band in MeOH···O=C with respect to the molecule of methanol also turned out to be much larger than in MeOH···O=S: 107 and 28 cm^{-1} respectively. Another important factor is the preferable *ap*-configuration of the amide group. For example, it is known that the *trans*-isomers of *N*-methylformamide and *N*-methylacetamide are by ~2 kcal mol^{-1} more stable than the corresponding *cis*-isomers [22]. This energy difference nicely coincides with the energy difference between dimers **IIa** and **IId** of 4.15 kcal mol^{-1} (Table 1) containing the same chelate cycles and differing only by configuration of the two amide fragments. In dimer **IIb** a larger strength and a smaller length of the two intermolecular hydrogen bonds NH···O=C forming the chelate cycle, as compared to NH···O=S in dimer **IIa**, practically level out the losses of energy due to the *sp*-configuration of the amide group and, eventually, dimers **IIa** and **IIb** have virtually the same energy (Table 1).

Theoretical and experimental estimation of the proton-donating ability of imide **I** was performed on the example of its interaction with DMF, acetonitrile and dioxane as bases. Nonvalent distances NH···O in the two latter complexes (Fig. 4) are by 0.15–0.16 Å larger than in the similar H-complexes of bis(trifluoromethanesulfonyl)imide $(CF_3SO_2)_2NH$, which is in line with its larger acidity [11]. The values of spectroscopic acidity Δν(NH), the difference between the vibration frequencies of the free and the associated with the Lewis base NH groups, were defined from the IR spectra upon addition of the corresponding base to the diluted solution of compound **I** in CCl_4 (Table 2). The formation of the H-complex of compound **I** with the standard base DMF causes the shift of the vibration band of the associated NH groups by more than 300 cm^{-1} and as a result it overlaps with the ν(CH) bands of the phenylacetyl substituents. In the spectrum of the H-complex of DMF with *N*-methyltrifluoromethanesulfonamide CF_3SO_2NHMe (**IV**) which is a stronger hydrogen bond donor than phenol or 4-fluorophenol being inferior only to 4-nitrophenol [23], the value of Δν(NH) is 272 cm^{-1}. The value of Δν(NH) exceeds 300 cm^{-1} also for interaction of compound **I** with dioxane, whereas for **IV** it is equal to 243 cm^{-1}. For the H-complexes of compounds **I** and **IV** with such a weak base as acetonitrile the value of Δν(NH) is equal to 186 and 137 cm^{-1} respectively. The calculated values of Δν(NH) for the H-complexes of compounds **I** and **IV**



ΔE_H –7.6 kcal mol^{-1}, Δν 202 cm^{-1} ΔE_H –10.5 kcal mol^{-1}, Δν 364 cm^{-1}

Fig. 4. Molecular structure of complexes of trifluoro-*N*-(2-phenylacetyl)methanesulfonamide with acetonitrile and dioxane.

with dioxane and acetonitrile are in good agreement with those found experimentally (Table 2, Fig. 4). Therefore, the data of quantum-chemical calculations and IR spectroscopy suggest that the NH acidity of trifluoro-*N*-(2-phenylacetyl)methanesulfonamide **I** in its interaction with the Lewis bases exceeds that of *N*-methyltrifluoromethanesulfonamide (**IV**). This is reflected in a high strength of the NH···O=S bonds in the cyclic dimer of the former compound.

EXPERIMENTAL

Synthesis of trifluoro-*N*-(2-phenylacetyl)methanesulfonamide **I** was described previously [8]. Quantum-chemical calculations including calculation of vibration frequencies was performed at the B3LYP/6-311G** level with a full geometry optimization using the Gaussian03 program package [24]. IR spectra of crystalline compound **I** (KBr pellets) and its solutions were registered on a Varian 3100 FT-IR spectrophotometer. The acidity of compound **I** was measured by the method of potentiometric titration using 0.1 N solution of NaOH in methanol as a titrant.

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