ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 2, pp. 315–322. © Pleiades Publishing, Ltd., 2009.
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Structure and Proton Donating Ability of 2- and 2,5-Bis(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)pyrroles

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Received June 15, 2008

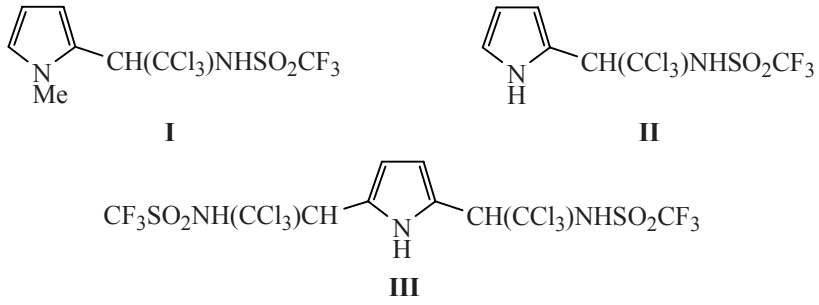
Abstract—2-(1-Trifluoromethanesulfonylamido-2,2,2-trichloroethyl)pyrrole and 2,5-bis(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)pyrrole according to quantum chemical calculations (B3LYP/6-311G**) exist in the isomeric forms whose structure determines the formation of intramolecular hydrogen bonds NH···Cl, NH···O=S and CH···O=S of different strength. Potentiometric and spectroscopic acidity of these compounds is determined. From the data of IR spectroscopy their proton donating ability upon interaction with Lewis bases is shown depending on the presence of intramolecular hydrogen bonds, mutual effects of intermolecular hydrogen bonds formed by the sulfonamide and pyrrole NH groups with the base, and electronic effects of the substituents.

DOI: 10.1134/S107036320902025X

Perfluoroalkanesulfonamides and their derivatives R_FSO_2NHR are characterized by high NH-acidity (pK_a for CF_3SO_2NHR (R = H, Me) 6.2–7.6 in water [1, 2] and 11.1–12.7 in methanol [3]) that causes the formation of strong intermolecular hydrogen bonds NH···O=S in crystals, which are retained even in the gas phase up to 440 K [4, 5]. In solution, the supramolecular structure of these compounds is determined by the properties of the medium. Presence of two trifluoromethanesulfonamide residues in the molecule allows the formation of intramolecular hydrogen bonds of various types as, for example, in bis(trifluoromethanesulfonylamino)methane $CF_3SO_2NHCH_2NHSO_2CF_3$; the compounds of this type exist in an inert medium as a mixture of monomeric forms rather than associates, the percentage of each form being dependent on the polarity of the solvent [3].

Recently, we have prepared 2-(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)pyrrole (**II**) and 2,5-bis(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)pyrrole (**III**) by the reaction of chloral trifluoromethanesulfonylimine $CF_3SO_2N=CHCCl_3$ with pyrrole [6] and performed theoretical analysis of regioselectivity of the reactions of C-amidomethylation of pyrrole with various sulfonylimines, including chloral trifluoromethanesulfonylimine [7]. The presence in the molecules of compounds **II** and **III** of acidic NH groups of the two types: pyrrole and sulfonamide, as well as of several centers of basicity (oxygen and halogen atoms) makes them interesting as the objects for investigation both from the viewpoint of NH-acidity and of homo- and heteroassociation due to formation of intra- and intermolecular hydrogen bonds in the presence of an external base. In the present work using the methods of IR spectroscopy and quantum chemical calculations for compounds **II** and **III** as well as for the hitherto unknown N-methylsubstituted analog of compound **II**, 2-(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)-1-methylpyrrole (**I**), we have studied their structure in the isolated and crystalline state and in inert media, the proton donating ability (spectroscopic NH-acidity) upon intermolecular interaction with Lewis bases, and determined the acidity of compounds **II** and **III** in methanol by potentiometric titration.

Compounds **II** and **III** show high NH-acidity, their pK_a values in methanol are 9.32 and 9.68, respectively. On the curve of potentiometric titration of amide **II** with NaOH solution in methanol only one kink is



observed, that is, under these conditions only the sulfonamide group SO_2NH is titrated and not the pyrrole NH group. Amide **III** is titrated with two equivalents of the base but on the potentiometric curve also only one kink is observed that implies that the first and the second constants of dissociation of this dibasic NH-acid are similar. Probably, this is due to remoteness of the NH groups separated by six bonds from each other and low sensitivity of one acidic center to emerging of the charge on the other center. The acidity of compounds **II** and **III** is substantially higher than for the earlier studied analogs CF_3SO_2·NHR (R = H, Me, $CH_2NHCOMe$, $CH_2NHSO_2CF_3$) for which the values of pK_a in methanol lie in the range of 10.1 – 12.7 pK_a units [3]. Apparently, this is first of all due to strong electronoacceptor effect of trichloromethyl group (σ* = 2.48 [8]), as well as electronoacceptor effect of the 2-pyrrolyl residue. We failed to find the value of σ* for the latter but the constants of dissociation of benzoic and 2-pyrrolylcarboxylic acids are close, 4.2 and 4.45 [9], that means that σ* for the 2-pyrrolyl group is equal to ~0.5.

Apart from the electronic effects of substituents, an important factor affecting the structure and acidity of compounds CF_3SO_2NHR in solution, as was shown in [3], is nonvalent intramolecular interactions. To establish the nature of such interactions we have performed quantum chemical calculations of molecules **I–III** at the B3LYP/6-311G** level of theory.

The isolated molecule **I** according to calculations has the structure in which interatomic distances H···X (X = Cl, O) (NH···Cl and CH···O=S) are less than the sum of the van der Waals radii of the corresponding atoms (2.95 and 2.72 Å) (Fig. 1). Here, the NH···Cl fragment having the length of the nonvalent bond of ~2.9 Å (Table 1) should be considered as a reduced interatomic contact rather than an intramolecular hydrogen bond (intra-HB). The value of ν(NH) of 3590 cm^{-1} in its calculated vibrational spectrum (Table 1) somewhat exceeds the frequency of vibrations of the free group ν(NH) 3580 cm^{-1} of *N*-methyltrifluoromethanesulfonamide CF_3SO_2NHMe (**IV**). This high-frequency shift is explained by electronoacceptor effect of the pyrrole ring and trichloromethyl group in compound **I**.

In IR spectra of solutions of compound **I** in CCl_4 (Table 2) the stretching vibrations of the NH group of

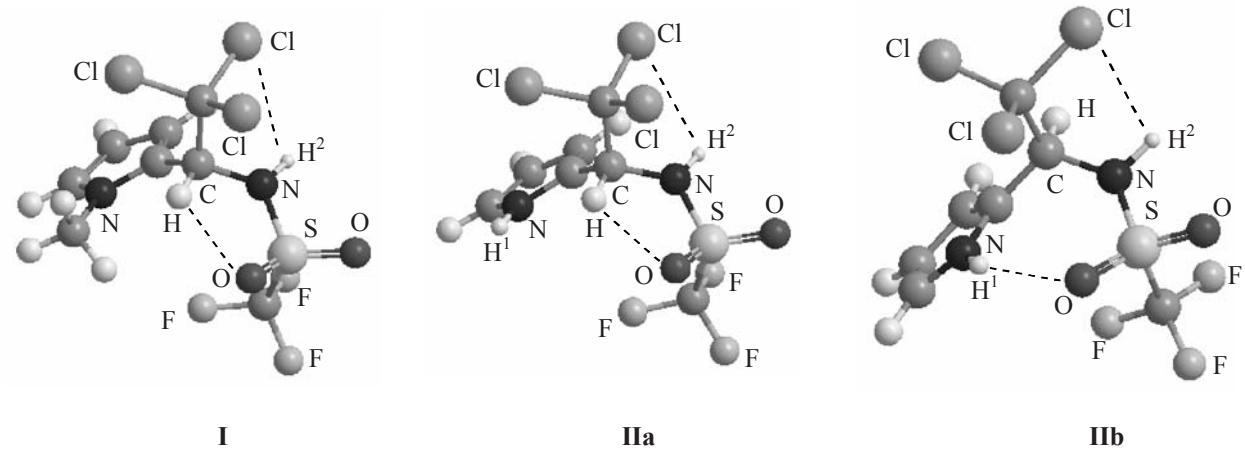


Fig. 1. Molecular structure of 2-(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)-1-methylpyrrole **I** and stereoisomers of 2-(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)pyrrole (**IIa**, **IIb**).

the sulfonamide fragment are characterized by bands at 3375 and 3280 cm^{-1}. With decrease of concentration of the solution the peak intensity of the high-frequency band increases whereas that of the low-frequency drops. Earlier it was shown that amide **IV** under similar conditions represents an equilibrium mixture of monomeric molecules and cyclic dimer characterized by frequencies ν(NH) 3407 and 3316 cm^{-1}, respectively [5]. This gives grounds to assign the band at 3280 cm^{-1} in the spectrum of compound **I** to vibrations of the NH group also participating in the formation of the cyclic dimer by means of two intermolecular hydrogen bonds NH···O=S (inter-HB). The high-frequency band ν(NH) at 3375 cm^{-1} belongs to monomeric molecule **I**. Its low-frequency shift by 32 cm^{-1} with respect to the band of the free NH group of amide **IV** is, apparently, due to sensitivity of ν(NH) vibrations to effects of the medium. Indeed, in the solution of compound **I** in polar CH_2Cl_2 the high-frequency band ν(NH) of its monomeric molecule at 3336 cm^{-1} is even more (by 44 cm^{-1}) shifted to low frequencies as compared to the band in the spectrum of amide **IV**. An intense band ν(NH) at 3271 cm^{-1} in the IR spectrum of crystalline compound **I** corresponds to its chain polyassociates with NH^{2}···O=S bonds which are also present in pure amide **IV** [5]. Its low-frequency shift by 30 cm^{-1} with respect to the IR spectrum of amide **IV** in thin layer can be related with higher strength of the inter-HB in compound **I** and/or different aggregate

Table 1. Calculated values of interatomic distances *d*(H···X) X = Cl, O of intramolecular hydrogen bonds (intra-HB) CH···O=S, NH···Cl and NH···O=S, Å, differences of energies Δ*E,* kcal mol^{-1}, dipole moments μ, D, and frequencies ν(NH), cm^{-1} of the studied compounds (B3LYP/6-311G**)

Comp. no.	Intra-HB	*d*(H···X)	Δ*E*	μ	ν(NH)
I	NH···Cl	2.865		4.39	3590 (48)
	CH···O=S	2.386			
IIa			0	4.33	3660 (64)
	NH^{2}···Cl	2.868			3593 (49)
	CH···O=S	2.402			
IIb	NH^{1}···O=S	2.105	1.5	2.73	3633 (133)
	NH^{2}···Cl	2.677			3571 (63)
IIIa	NH^{1}···Cl	2.574	0	1.82	3636 (85)
	CH···O=S	2.331			
	NH^{2}···Cl^{1}	2.946			3559 (36)
	CH···O=S	2.368			
	NH^{3}···Cl^{2}	2.830			3597 (56)
IIIb	NH^{1}···O=S	2.085	1.6	2.88	3592 (134)
	NH^{2}···Cl	2.687			3569 (70)
	CH···O=S	2.331			
	NH^{3}···Cl	2.944			3557 (37)
IV				4.18	3580 (56)
V				1.94	3674 (61)

Table 2. Frequencies of stretching vibrations (ν, cm^{-1}) of N–H bonds and values of Δν(NH) as differences between the value of ν(NH) of monomeric molecule in CCl_4 (or CH_2Cl_2) solution and of its H-complex with the base

Comp. no.	ν(NH)			Δν(NH)			
				solution in CCl_4[a]		solution in CH_2Cl_2[b]	
	CCl_4	CH_2Cl_2	KBr	dioxane	DMF	dioxane	DMF
I	3375	3336		296	315	276	>290
	3280		3271				
II	3476	3458	3442	160 (196)	110 (210)	150	115
			3380				
	3375	3335		260 (290)	260 (290)	230	>230
	3280		3274				
III		3437	3435			126 (130)	
		3321	3288			90 (100)	
		3255	3263				
IV	3407	3380		243 (270)	272 (310)	232	288
	3316		3300[в]				
V	3496	3476	3403[в]	113 (142)	140 (160)	126	166

[a] The values for solutions in pure bases are given in parentheses. [b] Thin layer.

states of amides **I** and **IV**, that is, with packing effects in the crystal. Therefore, in nonpolar inert medium the molecules of compound **I** exist in equilibrium with cyclic dimers, whereas in the solid state they are represented by chain polyassociates.

For molecule **II** the calculations give two conformers corresponding to minima on the potential energy surface (Fig. 1, Table 1). Conformer **IIa** along with the free NH_1 group of the pyrrole fragment contains the NH_2 group of the sulfonamide fragment having a reduced contact $NH^2\cdots Cl$ (2.873 Å), and the CH group forming a weak intra-HB $CH\cdots O$ (2.401 Å). This conformer is 1.5 kcal mol^{-1} more stable than conformer **IIb** with intra-HB $NH^1\cdots O{=}S$ (2.105 Å) and $NH^2\cdots Cl$ (2.677 Å). The values of the dipole moments 4.33 D (IIa) and 2.73 D **IIb** make conformer **IIa** to be better stabilized with increase of polarity of the medium. The calculated values of $\nu(NH^1)$ and $\nu(NH^2)$ reflect the structural peculiarities of conformers **IIa** and **IIb** (Table 1). Thus, the frequency of stretching vibrations of the free group NH^1 of the pyrrole fragment in **IIa** is by ~30 cm^{-1} higher than that of the same group participating in intra-HB $NH^1\cdots O{=}S$ in **IIb** and by 14 cm^{-1} lower than that of pyrrole. More strong intra-HB $NH^2\cdots Cl$ in **IIb** as compared to **IIa** is characterized by lower (by ~20 cm^{-1}) value of $\nu(NH_2)$.

In the IR spectra of solutions of compound **II** in CCl_4 the two vibration bands of the NH_2 group of the sulfonamide fragment (3375 and 3280 cm^{-1}) have the same frequencies and concentration dependence as in the spectrum of compound **I** (Table 2). Hence, the molecules of compound **II** in an inert nonpolar solvent also exist in the equilibrium between their monomeric form **IIa** and cyclic dimer closed by two inter-HB $NH^2\cdots O{=}S$. In the IR spectrum of the crystalline compound **II** an intense wide band at 3274 cm^{-1} corresponds to chain associates formed by inter-HB $NH^2\cdots O{=}S$. A narrow band of medium intensity at 3442 cm^{-1} in this spectrum is caused by vibrations of the free group NH_1 of the pyrrole fragment whereas a wide intense band at 3380 cm^{-1} belongs to vibrations of this group participating in the formation of intra-HB $NH^1\cdots O{=}S$. This conclusion is based of the values of $\nu(NH)$ in the spectrum of solution of unsubstituted pyrrole **V** in *N,N*-dimethyltrifluoromethanesulfonamide $CF_3SO_2\cdot NMe_2$ **VI**, which correspond to the monomeric molecule of pyrrole (3440 cm^{-1}) and its solvate complex with amide **VI** (3378 cm^{-1}). Probably, molecular crystals of compound **II** have two polymorphic forms. Their sulfonamide groups NH participate in the formation of chain associates with inter-HB $NH^2\cdots O{=}S$. The pyrrole NH group of form **IIa** participates in the formation of inter-HB $NH^1\cdots O{=}S$. In more curled and, probably, stabilized by crystal packing effects form **IIb** an intra-HB BBC $NH^1\cdots O{=}S$ with participation of the pyrrole NH group is realized that prevents its participation in formation of intermolecular H-bonds.

2,5-Bis(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)pyrrole (**III**), as was shown earlier by ^1H NMR spectroscopy [7] in DMSO-d_6 solution represents the mixture (~6:1) of diastereomers. According to calculations (B3LYP/6-311G**) [7] in the gas phase the *meso*-form (*R,S*) is 1.6 kcal mol^{-1} more stable but its dipole moment (1.82 D) is somewhat less than for the (*R,R*)-diastereomer [or identical to it (*S,S*)-diastereomer shown in Fig. 2] (2.88 D), so that the relative stability can depend on the nature of the solvent. SCRF//B3LYP/6-311G** calculations of the structures optimized at the same level of theory showed that in methylene chloride the value of ΔE is equal to 2.5 kcal mol^{-1} in favor of the *meso*-form, as is the case in the gas phase. This allowed us to assume that in solution the (*R,S*)-diastereomer is the major one whereas the minor component is a racemic mixture of enantiomers (*R,R* + *S,S*).

For both diastereomers the calculations give intramolecular hydrogen bonds (Fig. 2). In the *meso*-form (*R,S*) (**IIIa**) the H-bonds $CH\cdots O{=}S$ are formed in both side chains. The pyrrole NH atom in **IIIa** forms intra-HB $NH^1\cdots Cl$ (2.574 Å) with one of the side chains in which there is also a slightly reduced $NH^2\cdots Cl$ contact (2.946 Å) with the same chlorine atom. In another side chain the contact $NH^3\cdots Cl$ is somewhat shorter (2.830 Å). The calculated value of $\nu(NH_2)$ is by 40 cm^{-1} lower than $\nu(NH_3)$.

Unlike in the *meso*-form (**IIIa**), in the (*S,S*)-diastereomer (**IIIb**) the pyrrole NH atom forms intra-HB $NH\cdots O{=}S$ (2.085 Å) with one of the side chains; in the same chain an intra-HB $NH^2\cdots Cl$ (2.687 Å) is realized. In another side chain a slightly reduced contact $NH^2\cdots Cl$ (2.944 Å) and intra-HB $CH\cdots O{=}S$ (2.331 Å) are realized.

In the IR spectrum of the solution of compound **III** in CH_2Cl_2 (the compound in insoluble in CCl_4) the vibration frequency of the pyrrole NH group $\nu(NH_1)$ is by 20 cm^{-1} lower than that corresponding to vibrations of the free group NH_1 of compound **II** (Table 2). The presence of the intra-HB $NH^1\cdots Cl$ in form **IIIa**

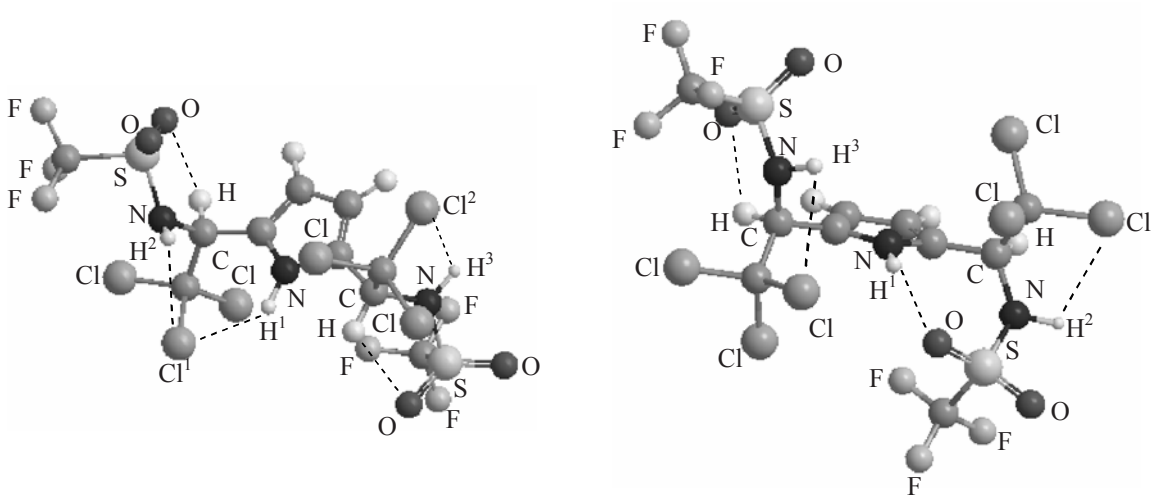


Fig. 2. Molecular structure of stereoisomers of 2,5-bis(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)pyrroles (**IIIa, IIIb**).

accounts for the observed low-frequency shift corresponding to the calculated one. The equal and rather high values of $\nu(NH_1)$ in the spectra of the crystalline disubstituted pyrrole **III** and its solution in CH_2Cl_2 (~3435 cm^{-1}) are indicative of the fact that the pyrrole NH atom forming the intra-HB with the chlorine atom does not contribute to the inter-HB with the oxygen atom of the sulfonyl group. It should be mentioned that the inter-HB $NH^1\cdots O{=}S$ with participation of the pyrrole NH atom in compound **II** are formed provided that the NH1 group is free and it causes a decrease of its vibration frequency to 3380 cm^{-1}. An intense doublet band with maxima at 3288 and 3263 cm^{-1} characterizes the two amide groups NH of the solid compound **III** participating on the formation of intermolecular associates. The band keeps its doublet shape in the spectrum of the solution of this compound in CH_2Cl_2. Its high-frequency component (3321 cm^{-1}) belongs to the NH_3 group which is not involved in the formation of inter-HB because of formation of intra-HB $NH^3\cdots Cl$. The low-frequency maximum at 3255 cm^{-1} belongs to the amide group NH2 which shows only a reduced contact $NH^2\cdots Cl$ and, therefore, participates in the formation of inter-HB $NH^2\cdots O{=}S$.

The proton donating ability of compounds **I–III** in CCl_4 and CH_2Cl_2 solutions was determined from the values of spectroscopic acidity $\Delta\nu(NH)$ as the difference between the values of $\nu(NH)$ for monomeric molecules in an inert solvent and their H-complexes formed in solution upon addition of Lewis bases (dioxane, DMF) (Table 2).

According to the data obtained, the proton donating ability of the sulfonamide group of compound **I** upon its interaction with dioxane and DMF is substantially higher that that of amide **IV**. This can be explained by electronoacceptor effect of the 1-methylpyrrole and trichloroethyl substituents. With this, *N*-methyltrifluoromethanesulfonamide **IV** itself, as we have shown earlier [10], in the H-complexes with protophilic solvents behaves as a strong hydrogen bond donor exceeding 4-fluorophenol and being second only to 4-nitrophenol. An increase of the $\Delta\nu(NH)$ value by 40–50 cm^{-1} in the H-complexes of compound **I** with respect to similar complexes of amide **IV** takes place in both inert solvents (CCl_4 and CH_2Cl_2), the low-frequency shift of the $\nu(NH)$ band for these compounds being larger for DMF as a base.

Dioxane and DMF interact with the molecule of the 2-substituted pyrrole **II** at two proton donor centers as witnessed by low-frequency shift of the vibrations bands of both the amide and the pyrrole NH groups. The values of $\Delta\nu(NH)$ for the H-complexes with participation of more acidic amide proton are by ~100 cm^{-1} larger than those of the pyrrole NH group. This is in line with the fact that spectroscopic acidity of *N*-methyltrifluoromethanesulfonamide **IV** upon its interaction with the same bases also turns out to be almost twice as large (by 110–130 cm^{-1}) as for the unsub-

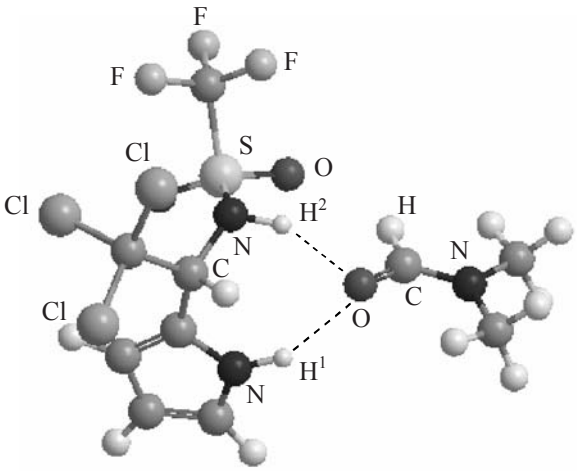


Fig. 3. Molecular structure of chelate H-complex of 2,5-bis(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)-pyrrole with DMF ($NH^1\cdots O{=}C$ 2.177Å, $NH^2\cdots O{=}C$ 1.947 Å).

stituted pyrrole **V** (Table 2). It must be noted that the values of Δν(NH) characterizing the amide group of compound **II** are by 40–50 cm^{-1} lower than those for compound **I** and, as distinct from compounds **I** and **IV** are practically equal for its complexes with dioxane and DMF. Structurally, the amide NH groups of the substituted pyrroles **I** and **II** are identical since both show reduced contacts NH···Cl with similar nonvalent distances. The calculated values of frequencies and intensities of the ν(NH) vibrations of the SO_2NH groups in isolated molecules **I** and **IIa** are identical. Also identical are the values of ν(NH) for these groups in the IR spectra of the solutions of compounds **I** and **II** in CCl_4 and CH_2Cl_2 (Table 2). Consequently, the observed decrease of the acidity of the amide hydrogen atom in compound **II** as compared to **I** is due to the effect of the H-bond formed by the base with the proton of its pyrrole group.

Spectroscopic acidity of the NH group of the pyrrole fragment of compound **II** upon interaction with dioxane is higher than that of pyrrole **V**: 160 and 113 cm^{-1} (CCl_4), 150 and 126 cm^{-1} (CH_2Cl_2) respectively, apparently, due to electronoacceptor effect of the substituent in the *2* position. A different behavior is observed in the case of more strong base, DMF. The values of Δν(NH) for the pyrrole NH group in this complex become lower than in the complex of pyrrole **V** with DMF: 110 and 140 cm^{-1} (CCl_4), 115 and 166 cm^{-1} (CH_2Cl_2), and also less than the values of Δν(NH) in the complex of compound **II** with more weak base, dioxane: 110 and 160 cm^{-1} (CCl_4), 115 and 150 cm^{-1} (CH_2Cl_2). Such a decrease of acidity of the proton of the pyrrolyl group of compound **II** is most probably due to variation of its conformational structure upon interaction with strong base in the CCl_4 solution. With this, the pyrrole and amide protons form H-bonds with the two lone pairs of the oxygen atom of one molecule of DMF thus closing the seven-membered chelate ring (Fig. 3). Judged from the calculations, the values of Δν(NH) for the pyrrole and amide groups in such a complex of compound **II** with DMF (80 and 230 cm^{-1}) deviate from the experimentally observed by only 30 cm^{-1} (110 and 260 cm^{-1}), and the difference between the values of $\Delta\nu(NH_1)$ and $\Delta\nu(NH_2)$ both in calculations and in the experiment is 150 cm^{-1}. At the same time, upon the formation of complex of compound **II** with two molecules of DMF these values amount to 230 and 460 cm^{-1} for the pyrrole and amide group, respectively, being different from the experiment. The length of the intermolecular H-bonds $NH^1\cdots O{=}C$ and $NH^2\cdots O{=}C$ in this 1:2 complex is 1.882 and 1.770 Å, respectively. It is noteworthy that the value of $\Delta\nu(NH_2)$ equal to 460 cm^{-1} is exaggerated owing to an additional H-bond closing the seven-membered ring between the CH group of DMF and the O=S group of molecule **II** with nonvalent distance H···O of 2.473 Å. Geometry optimization and vibrational calculations of the chelate complex of compound **II** with dioxane for slightly different distances $NH^1\cdots O$ (2.111 Å) and $NH^2\cdots O$ (2.125 Å) give close values of the spectroscopic acidity of the pyrrole and amide protons: $\Delta\nu(NH_1) = 113$, $\Delta\nu(NH_2) = 120$ cm^{-1}. These values are much less than the substantially different experimental values of 160 and 260 cm^{-1}, respectively.

The suggested chelate structure of the complex of **II** with DMF in which the oxygen atom of DMF participates in the formation of H-bonds with two hydrogen atoms is corroborated by comparing the values of Δν(NH) obtained for the spectra of solutions of compound **II** in pure bases. The difference between the values of Δν(NH) related to the pyrrole and amide groups in the dioxane solution remains unchanged as compared to the solutions in inert media (~100 cm^{-1}). In DMF solution, the value of $\Delta\nu(NH_2)$ for the amide hydrogen atom increases by 30 cm^{-1} with respect to CCl_4 solution, as is the case also for amide **IV**, and the value of $\Delta\nu(NH_1)$ for the pyrrole hydrogen atom increases from 110 to 210 cm^{-1}. The observed effect is consistent with the formation in pure DMF of the solvate complexes with two-centered intermolecular

hydrogen bonds NH···O=C involving two molecules of DMF which interact with the pyrrole and amide NH groups.

Proton donating ability of the pyrrole and amide groups of compound **III** (Table 2) was determined only with respect to dioxane in CH_2Cl_2 solution, since addition of DMF caused formation of the precipitate. The value of Δν(NH) for the pyrrole group NH_1 is 126 cm^{-1}, that is, much lower than for compound **II**, and is comparable to the similar H-complex of unsubstituted pyrrole **V**. A wide ν(NH) band of the amide groups in the H-complex of compound **III** with dioxane has maximum at 3230 cm^{-1} and its spectroscopic acidity Δν(NH) is as low as 90 cm^{-1}. This is possible in the case of formation of bifurcate (three-centered) hydrogen bonds when an intramolecularly H-bonded complex rather than the free amide group NH acts as an H-donor with respect to the external base (dioxane) [11]. The decrease of the proton donating ability of the pyrrole NH group of compound **III** with Δν(NH) 126 cm^{-1} as compared to the monosubstituted pyrrole **II** with Δν(NH) 150 cm^{-1} is apparently caused by participation of the two amide hydrogen atoms in the inter-HB with dioxane. The values of Δν(NH) for solution of compound **III** in pure dioxane calculated as the difference between ν(NH) of the monomeric molecule in CH_2Cl_2 solution and its H-complex in dioxane solution are only slightly different from those in the inert medium and are equal to 100 and 130 cm^{-1}. It is not inconceivable that a low value of Δν(NH) for the amide groups in compound **III** suggests the structure of its H-complex in which both these groups interact with the lone pair of one molecule of dioxane.

Therefore, the proton donating ability of the sulfonamide and pyrrole NH groups of 2- and 2,5-substituted pyrroles **I–III** is caused by electronic effects of the substituents in the molecules, influence of intermolecular H-bonds formed with Lewis bases, and the presence of intramolecular H-bonds.

EXPERIMENTAL

Quantum chemical calculations including vibrational calculations were performed at the B3LYP/6-311G** level with full geometry optimization using Gaussian 03 suit of programs [12].

IR spectra of pure compounds (in KBr or thin layer) and of their solutions in CCl_4 and CH_2Cl_2 were recorded on a Varian 3100 FT–IR spectrophotometer. ^1H, ^{13}C NMR spectra were registered on a Bruker DPX-400 spectrometer (400.13 and 100.62 MHz) in DMSO-d_6, chemical shifts are given with respect to tetramethylsilane. The acidity of amides **II** and **III** in methanol was determined by the method of potentiometric titration on a EV 74 ionomer with glass working electrode and chlorosilver electrode as a reference electrode using 0.1 N solution of NaOH in methanol as a titrant. Compounds **II**, **III** were prepared as described in [6].

2-(1-Trifluoromethanesulfonylamido-2,2,2-trichloroethyl)-1-methylpyrrole (I). To the solution of 0.01 mol of chloral trifluoromethanesulfonylimine $CF_3SO_2N{=}CHCCl_3$ prepared *in situ* [13] in 10 ml of trichloroethylene the solution of 0.01 mol (0.81 g) of 1-methylpyrrole in 3 ml of CCl_4 was added upon cooling with cold water. The reaction mixture was kept at room temperature for 6 h, solvent removed in vacuum. From the NMR data, the residue represents the mixture of product **I** and its isomer, 3-(1-trifluoromethanesulfonylamido-2,2,2-trichloroethyl)-1-methylpyrrole in the ratio of 9:1. The total yield 3.06 g (85%). Compound **I**. Yield 2.56 g (71%), m.p. 124–125°C (from hexane). ^1H NMR, δ, ppm: 3.64 s (3H, CH_3), 5.22 s (1H, CH), 6.03 m (1H, H^4), 6.57 m (1H, H^3), 6.81 m (1H, H^5), 11.12 br. s (1H, NH). ^{13}C NMR, δ, ppm: 33.78 (CH_3), 64.56 (CH), 101.10 (CCl_3), 107.19 (C^4), 110.28 (C^3), 119.16 q (CF_3, $^1J_{CF}$ 322.4 Hz), 124.08 (C^5), 124.56 (C^2). Found, %: C 26.91; H 2.27; Cl 29.15; N 7.64; S 9.04. $C_8H_8Cl_3F_3N_2O_2S$. Calculated, %: C 26.72; H 2.24; Cl 29.58; N 7.79; S 8.92.

3-(1-Trifluoromethanesulfonylamido-2,2,2-trichloroethyl)-1-methylpyrrole. ^1H NMR, δ, ppm: 3.60 s (3H, CH_3), 5.13 d (1H, ^3J 7.8 Hz, CH), 6.32 m (1H, H^4), 6.64 m (1H, H^5), 6.99 m (1H, H^2), 10.74 br. s (1H, NH). ^{13}C NMR, δ, ppm: 35.87 (CH_3), 67.68 (CH), 102.23 (CCl_3), 108.77 (C^4), 115.19 (C^3), 119.16 q (CF_3, $^1J_{C-F}$ 322.4 Hz), 121.61 (C^5), 122.72 (C^2).

Pure compound **I** was prepared by carrying out the reaction upon cooling to –15°C and crystallized from hexane.

***N,N*-Dimethyltrifluoromethanesulfonamide (VI)**. Autoclave was charged with 70 ml of trifluoromethanesulfonylfluoride and 60 g of dimethylamine (frozen in separate open vessels so that they were not mix before the autoclave was sealed otherwise the exothermic reaction with throwing out the reaction mixture occurs). The autoclave was closed, kept at room temperature for 1 day, cooled to 0°C, opened, the reaction mixture treated with dry ether (3×50 ml) and filtered. The

excess of dimethylamine was evaporated, the precipitate of dimethylamine hydrofluoride washed on filter with ether, solvent removed from the combined filtrate and the residue distilled in vacuum. Yield 67 g (82%). bp 42°C (12 mm) Hg. n_D^{20} 1.3658. d_4^{20} 1.374. ^{1}H NMR, δ, ppm: 3.06 s (6H, CH_3). ^{13}C NMR, δ, ppm: 37.94 (CH_3), 120.42 q (CF_3, $^1J_{CF}$ 320.5 Hz). ^{19}F NMR, δ, ppm: –75.95. Found, %: C, 20.99; H, 3.74; N, 7.92; S, 18.29; F, 32.36. $C_3H_6F_3NO_2S$. Calculated, %: C, 20.34; H, 3.41; N, 7.91; S, 18.10; F, 32.17.

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