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Intramolecular hydrogen bonds in the sulfonamide derivatives of oxamide, dithiooxamide, and biuret. FT-IR and DFT study, AIM and NBO analysis

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ABSTRACT

The hydrogen bonding in [(1-arylsulfonylamino-2,2,2-trichloro)ethyl]biuret **1**, [(1-arylsulfonylamino-2,2,2-trichloro)ethyl]oxamide **2**, and [(1-arylsulfonylamino-2,2,2-trichloro)ethyl]dithiooxamide **3**, the sulfonamide derivatives of biuret **4**, oxamide **5**, and dithiooxamide **6**, has been studied by molecular spectroscopy and DFT theoretical calculations including frequency calculations, at the B3LYP/6-311+G(d,p) level of theory. The analysis of the C=O···HN and C=S···HN intramolecular hydrogen bonds closing the five- and six-membered rings employing the atoms-in-molecules (AIM) method using the MP2(full)/6-311++G(d,p) wave functions has shown that their stability is increased in comparison to the original molecules and is much higher in the thiocarbonyl compounds. The results of the AIM and the NBO analysis of donor–acceptor interactions are in good agreement with each other and with the experimental FT-IR spectroscopy data.

1. Introduction

Compounds containing the amide or thioamide group are of great interest due to their biological activity.[1] Hydrogen bonding in these systems is the dominant interaction determining the conformation of the molecules and investigation of this may be helpful for peptide and protein structural characterization. Biuret and its derivatives are used as ligands in the synthesis of complex compounds.[2,3]

Recent quantum chemical studies of biuret and its thio-analogs have shown that the minima on the potential energy surface correspond exclusively to the *trans*-isomers, whereas the *cis*-isomers represent transition states.[4] The molecules exist predominantly in the diketo-form, although they are capable of tautomeric transformation to give the corresponding enols.[5] The presence of intramolecular hydrogen bonds plays an important role in these systems.[6] The sulfonamide group in unsaturated nitrogen-containing ligands results in a decrease of the σ-donating ability of the nitrogen atom lone pair and an increase of the π-acceptor properties of the chelating bidentate fragment.[7] In order to investigate the presence and the nature of hydrogen bonds in the sulfonamide derivatives of polyamide molecules, in the present work we have performed the FT-IR spectroscopic study and DFT theoretical calculations including the AIM and NBO analysis of [(1-arylsulfonylamino-2,2,2-trichloro)ethyl]biuret (**1**), [(1-arylsulfonylamino-2,2,2-trichloro)ethyl]oxamide (**2**), and [(1-arylsulfonylamino-2,2,2-trichloro)ethyl]dithiooxamide (**3**). A highly acidic SO_2NH group in these compounds is capable of forming strong hydrogen bonds.[8] All experimental measurements were performed for compounds **1b**–**3b**, whereas, without loss of generality, the unsubstituted analogs **1a**–**3a** were used for the theoretical analysis. The spectra of compounds **1b**–**3b** were compared to the spectra of the model compounds: biuret (**4**), oxamide (**5**), dithiooxamide (**6**) (rubeanic acid). We have also measured the NH-acidity of compounds **1b**–**3b** by potentiometric titration in methanol. Polyamide systems similar to **1**–**6** are used as strong NH acids,[9] reagents for asymmetric synthesis, and supramolecular chemistry,[10] in the synthesis of macrocyclic nitrogen-containing compounds.[11]

The structure and composition of compounds **1b**–**3b** was proved by FT-IR and ^1H, ^{13}C NMR spectroscopy, and elemental analysis.[12] The experimental frequencies ν_{NH} and ν_{CO} were assigned by comparing them with those derived from theoretical calculations of the vibrational spectra. The theory of atoms in molecules (AIM) was employed to indicate the existence and the relative strength of the intramolecular hydrogen bonds NH···O=C and NH···S=C closing the five- and six-membered rings in the studied molecules. The natural bond orbital (NBO) analysis was used to determine the importance of delocalization interactions in the conjugated fragments of the molecules.

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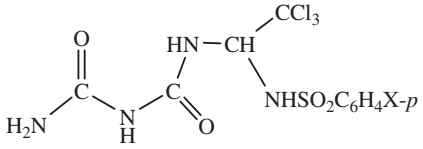
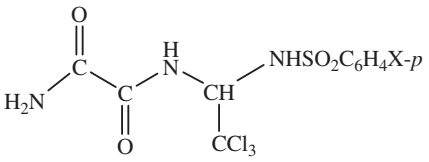


1a (X = H); **1b** (X = Cl).



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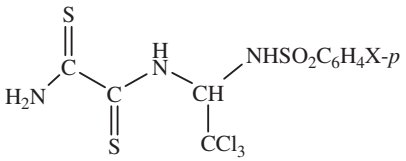
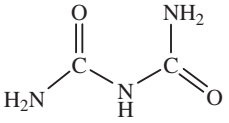


3a (X = H); **3b** (X = Cl).



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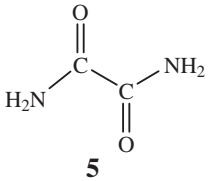

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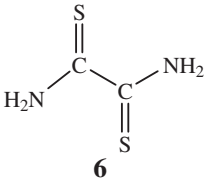

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2. Results and discussion

2.1. Potentiometric acidity

The sulfonamide derivatives **1**–**3**, as well as their model compounds **4**–**6** have two electron donating groups (C=O or C=S) and from two to four proton donor groups NH. Therefore, in the solid state they can exist as self-associates due to intermolecular hydrogen bonds and are also capable of formation of different intramolecular hydrogen bonds depending on the relative orientation of the donor and acceptor groups.

The values of pK_a of compounds **1b**–**3b** demonstrate rather high acidity of the SO_2NH group and are equal to 11.77, 11.18, and 11.69, respectively. They are more acidic than 4-chloro-*N*-[2,2,2-trichloro-1-(*p*-tolyl)-ethyl]benzenesulfonamide 4-$ClC_6H_4SO_2NHCH(Tol\text{-}p)CCl_3$ (pK_a 13.04) or *N*-methyltrifluoromethanesulfonamide (12.70),[13] although less acidic than trifluoromethanesulfonamide itself (pK_a 11.06) in the same solvent.[14] It is pertinent to mention that the potentiometric acidity of sulfonamides RSO_2NHR' is determined not only by the electronegativity of substituent R but also by nonvalent interactions in the molecule, including intramolecular hydrogen bonding.[14]

2.2. Geometry and FT-IR spectroscopy

In the early studies, a detailed analysis of the IR spectra of crystalline biuret and its thio-analogs in the region of the NH stretching vibrations was shown to be difficult.[15,16] Complete assignment was successfully made by the use of quantum chemical calculations of the vibrational spectra of these molecules and their deuterated analogs, and by invoking the experimental and theoretical spectra of formamide and thioformamide, whose FT-IR spectra were obtained in the gas phase and in the matrix-isolated state.[17]

We have analyzed the FT-IR spectra of compounds **1b**–**3b**, **4**–**6** in the solid state and in acetonitrile solution and compared them to the results of calculations (B3LYP/6-311+G(d,p)) of the vibrational frequencies of the isolated model molecules **1a**–**3a**, **4**–**6** (Table 1). All vibrational calculations were performed in the

Table 1
Experimental (FT-IR) and B3LYP/6-311+G(d,p) calculated frequencies of ν_{NH} and ν_{CO} vibrations of compounds **1**–**6** (for numbering of atoms see Fig. 1)

1b		**1a**		**4**			
ν_{exp}, cm^{-1}		ν^a_{calcd}, cm^{-1}	Mode assignment	ν_{exp}, cm^{-1}		ν^a_{calcd}, cm^{-1}	Mode assignment
Solid	MeCN			Solid	MeCN		
3446m	3472w	3710	$\nu^{as}(N1H_2)$	3402[b]vs	3486m	3710	$\nu^{as}(N1H_2)$
						3709	$\nu^{as}(N2H_2)$
3337w	3366m	3616	ν(N3H3)		3385m	3620	ν(N3H3)
		3591	$\nu^{s}(N1H_2)$			3591	$\nu^{s}(N1H_2)$
3270w	3310w	3494	ν(N4H4)	3250[b]s	3333w	3519	$\nu^{s}(N2H_2)$
3205m	3200m	3442	ν(N2H2)				
3140w							
1695s	1713s	1766	ν^{as}C=O+δNH_2	1725[b]vs	1712s	1792	ν^{as}(C=O)
(1701)[c]		1756	ν^{s}C=O+δN3H	(1690)		1764	ν^{s}(C=O)
2b		**2a**		**5**			
3379m	3461w	3712	$\nu^{as}(NH_2)$	3378m	—[d]	3713	$\nu^{as}(NH_2)$
3320m	3347m	3576	$\nu^{s}(NH_2)$	3177m		3573	$\nu^{s}(NH_2)$
		3548	ν(N2H2)				
3198m	3293m	3506	ν(N4H4)				
(1713)		1778	ν^{s}C=O+δNH_2	(1703)		1786	ν^{s}(C=O)
1661s	1706s	1744	ν^{as}C=O+δNH_2	1652s		1761	ν^{as}(C=O)
3b		**3a**		**6**			
3378m	3375w	3675	$\nu^{as}(NH_2)$	3286s	3375m	3677	$\nu^{as}(NH_2)$
				3204m			$2\delta(NH_2)$
3230m	3261m	3478	ν(N4H4)	3126s	3263m	3472	$\nu^{s}(NH_2)$
		3468	$\nu^{s}(NH_2)$				
3140w	3200w	3328	ν(N2H2)				

[a] Unscaled harmonic wavenumbers.
[b] Data for biuret-anhydrate from Ref. 17.
[c] The numbers in parentheses refer to the Raman frequencies.
[d] Compound is insoluble in MeCN.

harmonic approximation. The structures with the trans orientation of the carbonyl or thiocarbonyl groups were used for the geometry optimization, since, for example, the *cis*-form of biuret **4** is 12.3 kcal/mol less stable than its *trans*-form, and the *cis*-forms of oxamide **5** and dithiooxamide **6** do not correspond to minima on the potential energy surface (PES), and during the geometry optimization are transformed into the *trans*-forms.

In the IR spectrum of the solid compound **1b**, five stretching vibrational bands ν_{NH} are observed (Table 1). In solution, the lowest frequency band at 3140 cm^{-1} disappears, clearly pointing to its belonging to vibrations of the NH groups participating in the formation of an intermolecular hydrogen bond. Other ν_{NH} bands correspond to the free NH groups and to those involved in the intramolecular hydrogen bonds NH···O=C.

The global minimum on the PES of the model molecule **1a** corresponds to the structure with free NH_2 and NH groups, and with the amide and sulfonamide NH groups closing the two six-membered rings by formation of the NH···O=C intramolecular hydrogen bonds (Fig. 1). This form has the largest dipole moment (μ 10.06 D) and, hence, should be stabilized in polar media. Following the order of the calculated frequencies of molecule **1a** and comparing them to the experimental and calculated vibrational frequencies of biuret **4** (Table 1) we have made the assignment of the ν_{NH} and $\nu_{C=O}$ bands in the FT-IR spectrum of compound **1b** in solution. The highest frequency band at 3472 cm^{-1} belongs to the asymmetric stretch of the free NH_2 group in **1b**. In the spectrum of a solution of formamide, the similar band is located at 3480 cm^{-1} and in the spectrum of biuret **4** — at 3486 cm^{-1}. The next band in the FT-IR spectrum of **1b** at

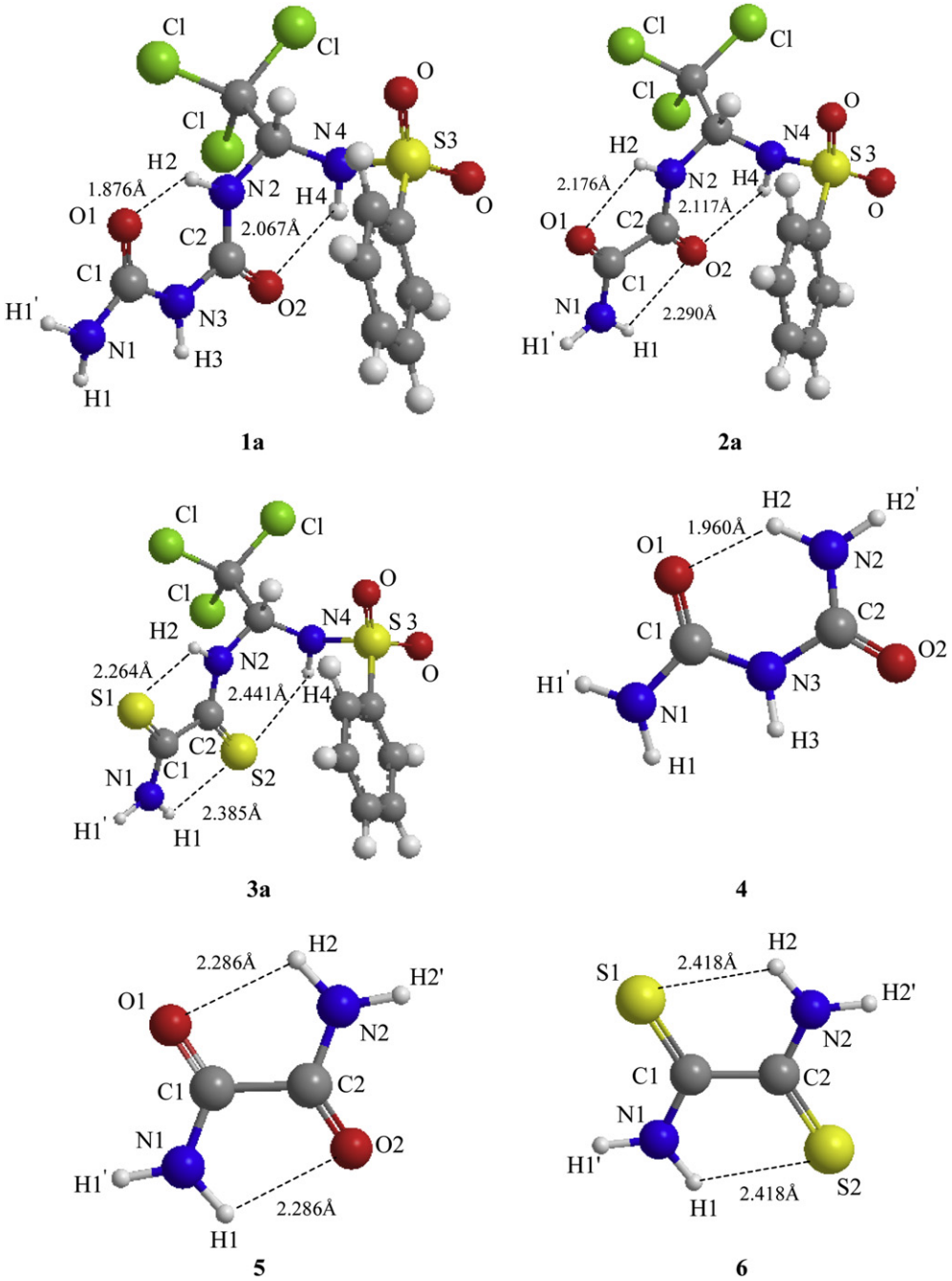

Fig. 1. B3LYP/6-311+G(d,p) calculated structures of molecules **1**–**6**.

3366 cm^{-1} corresponds to the stretching vibrations of the free NH group and symmetric stretch of the NH_2 group, as does the band at 3385 cm^{-1} in the FT-IR spectrum of biuret **4**. Their position corresponds to the values of ν_{NH} 3350–3360 cm^{-1} in the spectra of acetonitrile solutions of a wide series of acetanilides containing both electron donor and acceptor substituents in the benzene ring.[18] The bands relating to the vibrations of the sulfonamide and amide groups of **1b**, which according to calculations are involved in the formation of intramolecular hydrogen bonds appear at 3310 and 3200 cm^{-1}, respectively. Their relative positions correlate with the calculated H-bond lengths (l_{HO}) of the amide (l_{HO} 1.876 Å) and sulfonamide (l_{HO} 2.067 Å) groups NH in **1a** (Fig. 1). The single $\nu_{C=O}$ band at 1713 cm^{-1} in the spectrum of the solution of **1b** and at 1695 cm^{-1} in the spectrum of the solid sample corresponds to the stretching vibrations of the carbonyl groups involved in the formation of intramolecular hydrogen bonds. In the Raman spectrum of solid **1b** the bands of the carbonyl group stretching vibrations appear at 1701 cm^{-1}.

The relative stability of the intramolecular hydrogen bonds formed with participation of the amide and sulfonamide NH groups in compound **2** is different from that in **1**. In the most stable structure of the model compound **2a**, (μ 6.72 D) two five-membered rings are closed by the amide hydrogen bonds NH···O=C, whereas the sulfonamide NH group is involved in closing the six-membered ring (Fig. 1). The length of the H···O bond (l_{HO} 2.290 Å) formed by the NH_2 group is comparable with the length of the similar bond in oxamide **5** (l_{HO} 2.286 Å), both being 0.3 Å longer (and, hence, weaker) than the H-bond of the similar type in the six-membered ring of biuret **4**. The H-bond in the five-membered ring in molecule **2a** formed by the secondary amino group (l_{HO} 2.176 Å), although shorter than that with the primary amino group NH_2 by 0.1 Å, is still longer than the H-bond in the six-membered ring formed by the sulfonamide group (l_{HO} 2.117 Å). In the FT-IR spectrum of the acetonitrile solution of compound **2b**, the high frequency band ν^{as}_{NH2} appears at 3461 cm^{-1} (Table 1), as in the spectrum of compound **1b**, where this group is H-nonbonded. This also points to a weak intramolecular H-bond formed by the primary amino group in **2**. According to calculations and in analogy with the spectrum of solution of **1b**, a wide intense band at 3347 cm^{-1} is due to the stretching vibrations ν^{s}_{NH2} and ν_{NH} of the amide groups, and the lowest frequency band at 3293 cm^{-1} corresponds to the ν_{NH} vibrations of the sulfonamide group, which forms the shortest H-bond. In the calculated spectra of molecule **2a** and its molecular ancestor oxamide **5**, the inversion of asymmetric and symmetric stretching vibrations of the carbonyl groups occurs, and it is reflected in the IR and Raman spectra of the solid samples. The high frequency band appears in the Raman spectrum at 1713 (for **2b**) and 1703 cm^{-1} (for **5**) and belongs to the $\nu^{s}_{C=O}$ vibrations. The $\nu^{as}_{C=O}$ vibration band in the IR spectra of solid compounds **2b** and **5** appear at 1661 and 1652 cm^{-1}, respectively, whereas in the solution of **2b** the frequency of $\nu^{as}_{C=O}$ is equal to 1706 cm^{-1}.

The molecular structure of [(1-phenylsulfonylamino-2,2,2-trichloro)ethyl]dithiooxamide **3a** is similar to that of its oxamide analog **2a** (Fig. 1) with the two five-membered rings closed by the NH···S=C hydrogen bonds and one six-membered ring closed by the NH···S=C hydrogen bond. The difference between compound **2a** and its dithio analog **3a** is that, while for **2a** the N4H4···O2 is the shortest hydrogen bond in the molecule, for **3a** the H-bond N4H4···S2 is the longest one (Fig. 1). Moreover, introduction of the $CH(CCl_3)NHSO_2Ar$ moiety into the molecule of oxamide **5** leads to elongation of the N1H1···O2 H-bond and contraction of the N2H2···O1 H-bond, while for dithiooxamide **6** it results in contraction of both the N1H1···S2 and N2H2···S1 H-bonds. This is reflected in the order of the experimental ν_{NH} frequencies (Table 1).

To conclude this section, a general remark should be made, that in spite of much lower pK_a values for sulfonamides relative to the similarly substituted amides (ΔpK_a reaches 7–8 units[19]) the H-bond formed by the amide NH group in the studied molecules is shorter than (in **1a**, **3a**) or comparable with (in **2a**) that formed by the sulfonamide NH group. This reflects the principal difference between the thermodynamic acidity determined by the stability of the corresponding anion, and the spectroscopic acidity, which is determined as the value of $\Delta\nu_{NH}$ and is a measure of a hydrogen bond donating ability. Moreover, for molecular systems containing intramolecular hydrogen bonds the value of $\Delta\nu_{NH}$ is determined not only by the proton donating ability of the NH acid itself but also by steric restrictions imposed by the arrangement of the acidic and basic centers in the molecule.

2.3. Atoms in molecules analysis

The AIM analysis was used to determine the presence of bond critical points (BCPs) of the intramolecular bonds NH···X (X=O, S) and to evaluate their energies. The most often used criteria of the existence of hydrogen bonding interactions are the electron density $\rho(r_c)$ and the Laplacian of the electron density $\nabla^2\rho(r_c)$ at the BCPs. These parameters for the intramolecular NH···X along with the lengths and angles of the corresponding hydrogen bonds in the studied molecules are given in Table 2.

Table 2
Bond lengths ($l_{H\cdots X}$, Å), bond angles (∠(NHX), deg), electron densities ($\rho(r_c)$, e/Å^3), Laplacians ($\nabla^2\rho(r_c)$, e/Å^5) at BCPs, and bond energies for hydrogen bonds ($E_{H\cdots X}$, kcal/mol) in molecules **1**–**4**, **6**

Molecule, H-bond	$l_{H\cdots X}$	∠(NHX)	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$E_{H\cdots X}$	$-G_c/V_c$
1a, N2H2···O1	1.876	135.6	0.217	2.805	8.6	1.033
N4H4···O2	2.067	125.0	0.154	2.009	5.4	1.104
2a, N4H4···O2	2.117	124.1	0.140	1.800	4.8	1.108
3a, N1H1···S2	2.385	113.1	0.149	1.592	4.6	1.058
N2H2···S1	2.264	121.7	0.187	1.676	6.0	0.954
N4H4···S2	2.441	126.7	0.132	1.273	3.8	1.042
4, N2H2···O1	1.960	129.4	0.182	2.466	6.8	1.093
6, NH···S	2.418	112.9	0.129	1.530	4.3	1.080

No BCP corresponding to the NH···O hydrogen bond was found for oxamide **5**, as distinct from its thio analog **6**, which has two identical BCPs the two NH···S hydrogen bonds. There is good correlation between the $\rho(r_c)$ and $\nabla^2\rho(r_c)$ values and the NH···X distances, which, in turn, correlate well with the corresponding ν_{NH} frequencies. Positive values of Laplacian $\nabla^2\rho(r_c)$ in Table 2 are indicative of depletion of electronic charge along the bond path, which is characteristic of closed shell interactions such as hydrogen bonds. The penultimate column in Table 2 shows the hydrogen bond energies calculated similar to[20]:

$$E_{H\cdots X} = 1/2V_c; \quad V_c = 1/4\nabla^2\rho(r_c) - 2G_c$$

where V_c is the local potential electron energy density and G_c is the local kinetic electron energy density. Finally, the last column gives the ratio $-G_c/V_c$, which was used as a criterion of the nature of H-bond:[20,21] for $-G_c/V_c>1$ the H-bond is noncovalent, while for $0.5<-G_c/V_c<1$ it is partly covalent.

As can be seen, in practically all cases the H-bonds in the systems under consideration are noncovalent, their values being very close to those obtained for N–H···O=C H-bonds.[20] The only exception is the N2H2···S1 H-bond in **3a**, which has a small covalent contribution. This is consistent with the largest value of $E_{H\cdots X}$ for this H-bond in **3a**, as well as with the strongest interaction $n_{S1}\rightarrow\sigma^*_{N2-H2}$ found by the NBO analysis (vide infra).

The abovementioned absence of BCP in **5** and its presence in **6** is presumably caused by two factors. First, the thiocarbonyl group is much more basic than the carbonyl group due to the lower

electronegativity and higher polarizability of sulfur versus oxygen.[22] Second, although the H···O distance in **5** is 0.13 Å shorter than the H···S distance in **6**, it is only 0.34 Å less than the sum of the vdW radii of H and O atoms, whereas the latter distance is 0.64 Å less than the sum of the vdW radii of H and S atoms.

2.4. NBO analysis

The NBO method was used for quantitative analysis of the electron delocalization from the lone pairs of the nitrogen and oxygen atoms to the adjacent antibonding π^* and σ^*-orbitals (Table 3).

As an independent characteristic of the NH···X hydrogen bond energy we have analyzed the second-order interaction energies $E^{(2)}$ between the donor orbitals (lone pairs on X) and acceptor orbitals (σ^*_{N-H}) forming the hydrogen bond. In **1a**, the value of $E^{(2)}$ for the $n_{O1} \rightarrow \sigma^*_{N2-H2}$ orbital interaction (10.84 kcal/mol) is notably larger than that in biuret **4** (6.82 kcal/mol). This is presumably due to the electron–acceptor effect of the $CH(CCl_3)NHSO_2Ph$ substituent since the positive NBO charge on H2 increases on going from biuret **4** to molecule **1a** by 0.021±0.001 e, thus favoring the N2H2···O1 H-bond formation. The N4H4···O2 H-bond in **1a** is characterized by much lower value of $E^{(2)}$ (4.70 kcal/mol) than the N2H2···O1 H–bond. The NBO charge on H4 is 0.008 e more positive than that on H2. Therefore, the main reason for the weaker N4H4···O2 relative to the N2H2···O1 H-bond lies in different geometry of the two H-bonded rings. The ring that includes the amide NH group is planar since all the constituting atoms are sp^2 hybridized. The presence of the sp^3 hybridized CH atom in the ring formed with participation of the sulfonamide NH group leads, first, to the lengthening of the corresponding N–CH bonds and, second, to nonplanarity of the ring and deviation of the NH group from the plane of the remaining four atoms. As a result, the N4H4···O2 H-bond becomes 0.192 Å longer (and, hence, weaker) than the N2H2···O1 H-bond.

Table 3
Second order perturbation energies $E^{(2)}$ (kcal mol^{-1}) for orbital interactions related to hydrogen bond formation in molecules **1**–**6**

Molecule	Interaction	$E^{(2)}$
1a	$n_{N1} \rightarrow \pi^*_{C1-O1}$	26.01
	$n_{N2} \rightarrow \pi^*_{C2-O2}$	65.82
	$n_{N3} \rightarrow \pi^*_{C2-O2}$	44.50
	$n_{N3} \rightarrow \pi^*_{C1-O1}$	34.15
	$n_{O1} \rightarrow \sigma^*_{N2-H2}$	10.84
	$n_{O2} \rightarrow \sigma^*_{N4-H4}$	4.70
2a	$n_{N1} \rightarrow \pi^*_{C1-O1}$	69.15
	$n_{N2} \rightarrow \pi^*_{C2-O2}$	70.71
	$n_{O1} \rightarrow \sigma^*_{N2-H2}$	1.63
	$n_{O2} \rightarrow \sigma^*_{N1-H1}$	0.69
	$n_{O2} \rightarrow \sigma^*_{N4-H4}$	3.74
3a	$n_{N1} \rightarrow \pi^*_{C1-O1}$	88.76
	$n_{N2} \rightarrow \pi^*_{C2-O2}$	91.98
	$n_{S1} \rightarrow \sigma^*_{N2-H2}$	11.63
	$n_{S2} \rightarrow \sigma^*_{N1-H1}$	4.74
	$n_{S2} \rightarrow \sigma^*_{N4-H4}$	5.78
4	$n_{N1} \rightarrow \pi^*_{C1-O1}$	8.08
	$n_{N2} \rightarrow \pi^*_{C2-O2}$	62.62
	$n_{N3} \rightarrow \pi^*_{C2-O2}$	42.32
	$n_{N3} \rightarrow \pi^*_{C1-O1}$	28.40
	$n_{O1} \rightarrow \sigma^*_{N2-H2}$	6.82
5	$n_{N1} \rightarrow \pi^*_{C1-O1}$	68.53
	$n_{N2} \rightarrow \pi^*_{C2-O2}$	68.53
	$n_{O1} \rightarrow \sigma^*_{N2-H2}$	0.80
	$n_{O2} \rightarrow \sigma^*_{N1-H1}$	0.80
6	$n_{N1} \rightarrow \pi^*_{C1-O1}$	87.80
	$n_{N2} \rightarrow \pi^*_{C2-O2}$	87.80
	$n_{S1} \rightarrow \sigma^*_{N2-H2}$	5.11
	$n_{S2} \rightarrow \sigma^*_{N1-H1}$	5.11

In **2a**, the values of $E^{(2)}$ for the $n_{O1} \rightarrow \sigma^*_{N2-H2}$ and $n_{O2} \rightarrow \sigma^*_{N1-H1}$ interactions are 7 and 15 times, respectively, less than in biuret **1a** (Table 3). The only more or less significant interaction is the one with the sulfonamide NH group (3.74 kcal/mol). This is consistent with the results of the AIM analysis, which finds only one BCP in **2a** belonging to the N4H4···O2 H-bond. Nonvalent interactions in the model compound **5** are practically negligible, which is also in line with the absence of the corresponding BCPs (vide supra).

On the example of formamides, ureas, biuret, isocyanates, and their thio analogs, the electron delocalization through covalent bonds in thioamides was shown to be more efficient than in amides, which was assigned to lower values of ΔE_{ij} and larger matrix elements of the Fockian F_{ij} determining $E^{(2)}$ by equation $E^{(2)}=-2F_{ij}/\Delta E_{ij}$.[5,23] As follows from the AIM and NBO analysis of compounds **1**–**6**, the same is true for the noncovalent hydrogen bonding interactions. The NBO analysis clearly shows (Table 3) that all three such interactions in **3a**, $n_{S1} \rightarrow \sigma^*_{N2-H2}$, $n_{S2} \rightarrow \sigma^*_{N1-H1}$, and $n_{S2} \rightarrow \sigma^*_{N4-H4}$, are much more efficient than the corresponding orbital interactions in **2a**, and the AIM analysis finds three BCPs corresponding to H-bonds in **3a** and only one in **2a**.

3. Conclusions

The experimental and theoretical study of hydrogen bonding in compounds **1**–**3** has shown them to be strong NH acids due to the presence of the sulfonamide group with the pK_a values in methanol of 11–12 units. They are also capable of forming intramolecular hydrogen bonds due to both the amide and the sulfonamide NH group with the carbonyl or thiocarbonyl group. The relative stability of these H-bonds depends on the structure of the centers of basicity in the molecule. For example, in compound **2a**, the sulfonamide group forms the shortest (and strongest) H-bond, whereas in compounds **1a** and **3a** it is the longest (and weakest) one. The AIM analysis showed that all H-bonds in molecules **1a**–**3a** are noncovalent, except the N2H2···S1 H-bond in **3a**, which has a small covalent contribution. No BCP corresponding to the NH···O H-bond was found for oxamide **5**, whereas for more basic dithiooxamide **6** each of the two NH···S H-bonds has BCP. The NBO analysis method showed that the second-order C=X···HN (X=O, S) interaction energy $E^{(2)}$, which is an independent characteristic of the NH···X H-bond energy, vary from 0.7 to 11.6 kcal/mol and correlate well with the hydrogen bond energies predicted by the AIM analysis and with the experimental FT-IR spectroscopy data.

4. Experimental section

4.1. General

Compounds **1b**–**3b** were synthesized by addition of biuret, oxamide, and dithiooxamide to 4-chloro-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide *p*-$ClC_6H_4SO_2N{=}CHCCl_3$.[12]

4.2. IR experiments

The FT-IR spectra were recorded on a portable diamond ATR/FT-IR (RAM II) Spectrometer Varian 3100. The potentiometric acidity of compounds **1b**–**3b** was measured by titration with 0.1 M NaOH solution in methanol.

4.3. Computational details

All calculations were performed by the DFT method using the B3LYP exchange correlation potential and the 6-311+G(d,p) basis set as implemented in the Gaussian03 program package.[24] All calculated structures correspond to minima on the potential energy

surface (PES) as proved by positive eigenvalues of the corresponding Hessian matrices. All energies were calculated with the ZPE correction. The AIM analysis[25] was performed by the use of the AIM2000 program (version 2.0)[26] with the wave function taken from the MP2/6-311++G** single point calculations. The NBO analysis[27] as implemented into the Gaussian03 package was performed using the 6-311+G** basis set on the previously DFT optimized structures. The van der Waals radii of H=1.20 Å, O=1.40 Å, and S=1.85 Å are used in the discussion.

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Supplementary data

Supplementary data includes synthetic details, NMR and IR spectra of the products, total energies, and optimized geometries of compounds **1**–**6**. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.08.076. These data include MOL files and InChIKeys of the most important compounds described in this article.

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