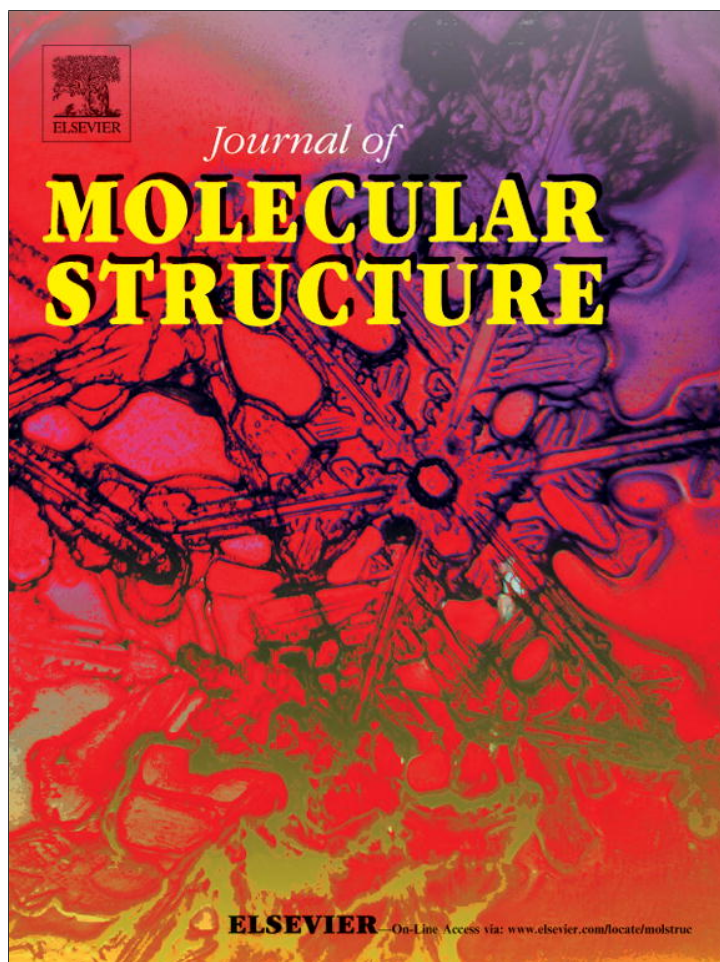


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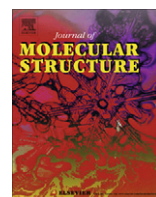
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Crystal structure and spectroscopic properties of *N'*-methoxycarbonylsulfonyl-substituted ureas, $\text{CH}_3\text{OC}(\text{O})\text{SN}(\text{H})\text{C}(\text{O})\text{NRR}'$ [$\text{R} = \text{H}$, $\text{R}' = -\text{C}(\text{CH}_3)_3$ and $\text{R} = \text{R}' = -\text{CH}_2\text{CH}_3$] [☆]

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HIGHLIGHTS

- ▶ N,N-diethyl- (**I**) and *N*-*tert*-butyl-*N'*-methoxycarbonylsulfonyl urea (**II**) have been prepared.
- ▶ Structural and spectroscopic properties of (**I**) and (**II**) have been analyzed.
- ▶ The conformation of the O—(C=O)—S—N—(C=O)—N skeleton of **II** is almost identical to the corresponding of **I**.
- ▶ Vibrational properties (FTIR and Raman) of (**I**) and (**II**) have been studied.
- ▶ The experimental study was complemented by using quantum chemical calculations.

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ABSTRACT

Structural and spectroscopic properties of N,N-diethyl- (**I**) and *N*-*tert*-butyl-*N'*-methoxycarbonylsulfonyl urea (**II**) are analyzed using a combined approach with data obtained from X-ray diffraction, vibrational spectra and quantum chemical calculations. The molecular structures of $\text{CH}_3\text{OC}(\text{O})\text{SN}(\text{H})\text{C}(\text{O})\text{N}(\text{CH}_2\text{CH}_3)_2$ (**I**) and $\text{CH}_3\text{OC}(\text{O})\text{SN}(\text{H})\text{C}(\text{O})\text{N}(\text{H})\text{C}(\text{CH}_3)_3$ (**II**), the later co-crystallized with ethyl acetate (**II** 1/2EtOAc), were determined by X-ray diffraction methods. Compound **I** crystallizes in the triclinic space group *P*-1 and **II**·0.5EtOAc in the orthorhombic space group *Pnma*. In **I**, there are two independent but closely related molecules in the asymmetric unit whose conformations differ only in the orientation of the terminal $\text{N}(\text{CH}_2\text{CH}_3)_2$ groups. Neighboring molecules in **I** exhibit $\text{N}-\text{H}\cdots\text{O}$ interaction giving rise to a polymeric chains. The conformation of the O—(C=O)—S—N—(C=O)—N skeleton of **II** is almost identical to the corresponding one of both molecules of **I**. Neighboring molecules in **II** are linked through bifurcated $\text{N}-\text{H}\cdots\text{O}\cdots\text{H}-\text{N}$ interactions giving rise to a polymeric chain. The vibrational properties have been studied by FTIR and FT-Raman spectroscopy along with quantum chemical calculations at the B3LYP/6-311+G* level.

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1. Introduction

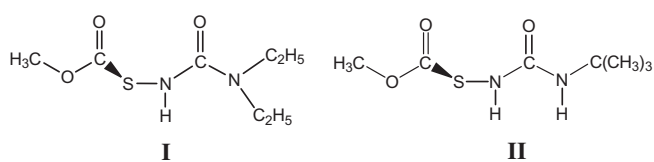
Urea has been extensively studied because it is one of the simplest biological molecules and also one of the simplest diamide precursors used in organic and pharmaceutical chemistry [1]. The

molecular properties of urea have been thoroughly investigated, both experimentally and theoretically [2]. $\text{NH}_2\text{C}(\text{O})\text{NH}_2$ contains C=O and N—H groups which can act as acceptor and donor hydrogen bonds between neighboring urea molecules in the solid state [3]. In fact, it has been found that the urea molecules usually form

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Scheme 1. N,N-diethyl- (**I**) and N-*tert*-butyl-N'-methoxycarbonylsulfonyl urea (**II**).

extensive networks of hydrogen bonds which confer the observed planar molecular conformation and result in motifs such as chains and ribbons [2,4].

N,N'-substituted ureas are also well-known species and a general procedure for their synthesis involves the reaction of isocyanates with primary or secondary amines [5]. These derivatives have also attracted considerable attention due to their specific structural features, in particular if the central —NH—C(=O)—NH— group remains planar upon substitution and especially because urea derivatives are good model compounds for the study of structural effects promoted by intra and/or intermolecular hydrogen bonding in the urea moiety [6]. However, N-substituted sulfonyl ureas, containing divalent sulfur atoms bonded to the amidic nitrogen atoms, are scarcely studied species and only a few examples are reported in the literature. They are obtained through the hydrolysis reaction of simple inorganic isocyanates of the type XC(O)SNCO ($\text{X} = \text{F}, \text{Cl}$) to yield the corresponding N,N'-di(halocarbonylsulfonyl)-substituted ureas $\text{XC(O)—SN(H)C(O)N(H)S—C(O)X}$ ($\text{X} = \text{Cl}, \text{F}$) [7]. In a previous work, we reported on the structural properties of the derivative with $\text{X} = \text{OCH}_3$ [8].

Recently, we published a method for preparing the new isocyanate $\text{CH}_3\text{OC(O)SNCO}$ [9]. This is a very versatile reagent for nucleophilic addition reactions, for example when amines are used [10]. In this context, we became interested in the structural study of molecules containing the —SN(H)C(O)N— group. Thus, we report here the X-ray structure determination and a vibrational analysis of the unsymmetrically substituted species N,N-diethyl- (**I**) and N-*tert*-butyl-N'-methoxycarbonylsulfonyl urea (**II**) (see Scheme 1).

2. Results and discussion

2.1. Quantum chemical calculations

In principle there are several conformers of the studied compounds, depending on the conformation adopted around each of the molecular single bonds. Previous structural studies reported for $\text{CH}_3\text{OC(O)SX}$ show that the *syn* orientation of both $\delta(\text{CO—C=O})$ and $\delta(\text{O=C—SX})$ dihedral angles is strongly preferred [11,12]. Moreover, it has been found that the orientation around the S—N single bond adopted for sulfonyl ureas is nearly *gauche* (90° or 270°) [13]. Thus, special attention was paid to the sulfonyl urea moiety, —SN(H)C(O)NR— . To investigate the potential energy hyper-surface describing the conformational space, *relaxed* potential energy curves at the B3LYP/6-31G* level have been calculated for internal rotation around the respective single bonds, namely S1—N11, N11—C13 for compound **I** and S1—N1, N1—C3, C3—N2 for compound **II**, as shown in the Supporting Information (Fig. S1). These curves indicate the preference of a mutual *syn* orientation of the S1—N11 single bond with respect to the C13=O13 double bond for compound **I** [$\delta(\text{S1N11—C13=O13}) = 10^\circ$]. For the rotation around the equivalent N1—C3 single bond in the sulfonyl urea group of compound **II**, the *syn* [$\delta(\text{S1N1—C3=O3}) = 0^\circ$] and *anti* [$\delta(\text{S1N1—C3=O3}) = 180^\circ$] conformers are found to be stable with similar computed electronic energies. These conformational features will be further discussed in connection with the X-ray crystal structure.

In a second step, the harmonic vibrational frequencies were obtained for the fully optimized geometries of the more stable conformers of the title compounds, N,N-diethyl- (**I**) and N-*tert*-butyl-N'-methoxycarbonylsulfonyl urea (**II**), at the B3LYP/6-311++G** level of approximation. The vibrational analysis enables the characterization of a given conformation as a true minimum on the molecular potential energy surface. Furthermore, the calculated harmonic frequencies are useful in the assignment of the experimental vibration data.

2.2. Vibrational analysis

The solid-state IR and Raman vibrational spectra of $\text{CH}_3\text{OC(O)SN(H)C(O)N(C}_2\text{H}_5)_2$ (**I**) and $\text{CH}_3\text{OC(O)SN(H)C(O)N(H)C(CH}_3)_3$ (**II**) are shown in Figs. 1 and 2, respectively. A tentative assignment of the observed bands was carried out by comparison with theoretical wavenumbers and with the spectra of related, simpler molecules [14,15]. Experimental and calculated [B3LYP/6-311++G**] frequencies and intensities are given as Supporting Information (Tables S1 and S2). The general features in the observed spectra of **I** and **II** can be explained by assuming the presence of only one conformer for each compound: *anti* (**I**) and *anti-anti* (**II**) conformer, respectively. The assignment of the characteristic vibrational modes of the main —C(O)SN(H)C(O)N— moiety is summarized in Table 1.

The intense IR absorptions at 3274 cm^{-1} (for **I**) and 3359 and 3250 cm^{-1} (for **II**) are assigned to the N—H stretching mode. The formation of $\text{C=O}\cdots\text{H—N}$ intermolecular hydrogen bonds seems to strongly affect the frequency of the $\nu(\text{N—H})$ mode involved in the formation of the H-bonds in compound **I** and the bifurcated hydrogen bonds formed in compound **II** in which the N—H bond affected by the formation of two hydrogen bonds shows a stretching frequency red-shift. For example, a strong band at 3247 cm^{-1} was observed in the IR spectra of the symmetric N,N'-di(methoxycarbonylsulfonyl) urea, a molecule which exhibits intermolecular hydrogen bonds [8].

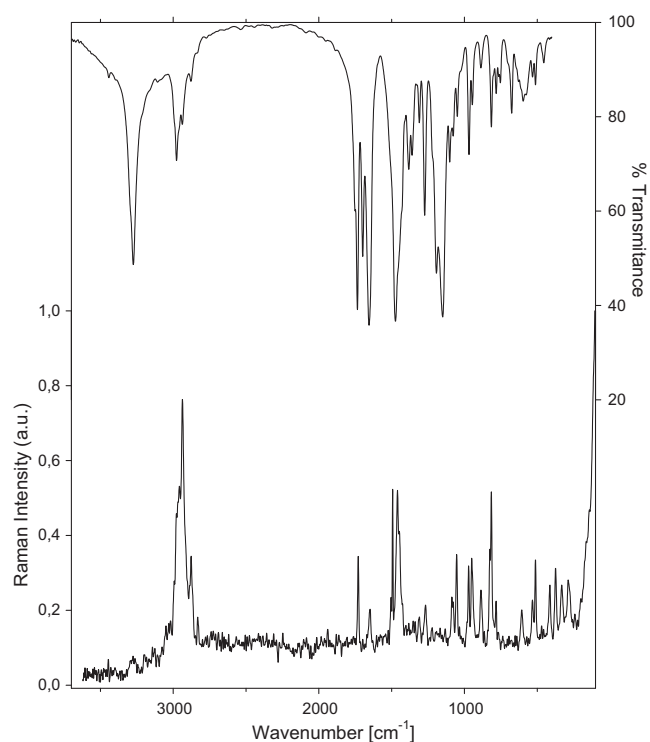


Fig. 1. Solid-state IR (sample in KBr pellet) absorption and Raman dispersion spectra for compound **I**.

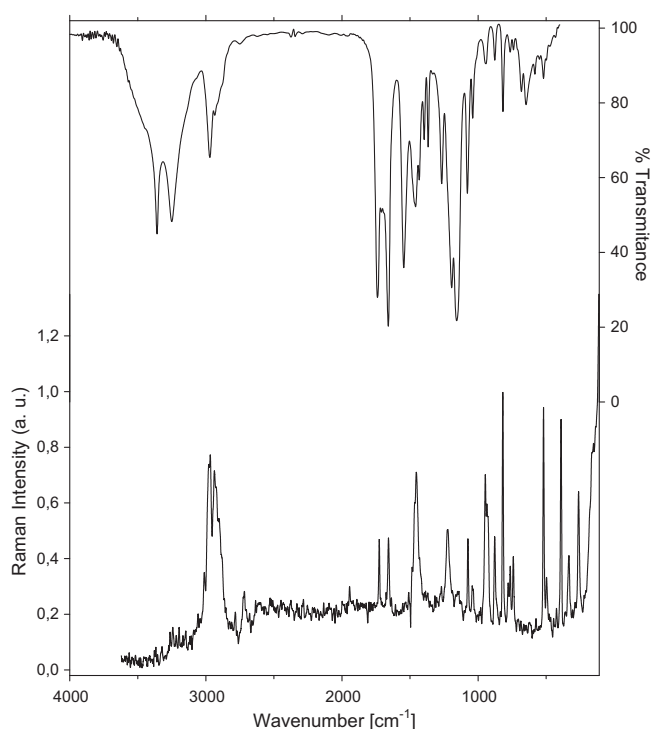


Fig. 2. Solid-state IR absorption (sample in KBr pellet) and Raman dispersion spectra for compound II.

As expected, two absorptions are observed in the carbonyl stretching region for both studied compounds. Thus, the strong IR absorptions at 1735, 1655 and 1741, 1659 cm^{-1} with counterparts in the Raman spectra at 1729, 1648 and 1726, 1658 cm^{-1} , respectively for compounds **I** and **II**, were assigned to the $\nu(\text{C}=\text{O})$ modes with the ones at the higher frequencies being assigned to the carbonyl group of the methoxycarbonyl part and the ones at lower frequencies to the urea group. The relatively low frequency values for the $\nu(\text{C}=\text{O})$ stretching mode of the urea moiety in the IR spectra of the compounds can be related to the formation of intermolecular hydrogen bonds involving the carbonyl group. Indeed, $\text{C}=\text{O} \cdots \text{H}-\text{N}$ bonds are observed in the solid-state structure of both studied compounds, as will be discussed in Section 2.3.

In connection with the urea group, a strong IR absorption at 1546 cm^{-1} for compound **II** is assigned to the in-plane N–H rocking mode [$\rho(\text{N}-\text{H})$]. Additionally, the counterpart of the urea

group linked to the sulfur atom in both studied molecules appears as strong absorptions at 1474 (**I**) and 1470 cm^{-1} (**II**) and are assigned to in-plane N–H rocking modes [$\rho(\text{N}-\text{H})$]. Similar values were reported recently for related thiourea species [16,17]. The most intense signal in the Raman spectrum of compound **I** appears at 2937 cm^{-1} and is assigned to the symmetric stretching mode of the methyl group [$\nu_s(\text{CH}_3)$] (see Table S1), whereas the most intense signal in the corresponding Raman spectrum of compound **II** at 818 cm^{-1} is assigned to the combined rocking modes of the methoxycarbonyl group of the molecule [$\rho(\text{O}-\text{C}=\text{O})$].

2.3. Solid-state structures

Compound I. There are two independent N,N-diethyl-N'-methoxycarbonylsulfenyl urea molecules in the asymmetric unit (Fig. 3). Selected bond lengths and angles are given in Table 2. Molecules of **I** exhibit N–H \cdots O interactions [$d(\text{N}21 \cdots \text{O}13) = 2.910(3) \text{ \AA}$, $\angle(\text{N}21-\text{H} \cdots \text{O}13) = 160.2(2)^\circ$] to dimers. The conformations of the monomers are nearly the same and similar to those of urea-free molecules for which Andrew and Hyndman have verified the planarity by proton magnetic resonance studies [18], except for a change in the orientation of the terminal $-\text{N}(\text{CH}_2\text{CH}_3)_2$ groups, which are approximately related to each other by a mirror plane defined by the $\text{S}(x)-\text{N}(x)-(\text{C}(x)3=\text{O}(x)3)-\text{N}(x)2$ ($x = 1$ or 2) skeleton (see Fig. 3). In fact, a least-squares structural fitting of both molecules by the Kabsch's procedure [18], including all but the methyl groups of the $-\text{N}(\text{CH}_2\text{CH}_3)_2$ groups, gives a *rms* deviation between homologous non-H atoms of 0.092 \AA . Neighboring dimers, symmetry-related through a [1–10] lattice translation, are in turn N–H \cdots O bonded to each other [$d(\text{N}11 \cdots \text{O}23') = 2.916(3) \text{ \AA}$, $\angle(\text{N}11-\text{H} \cdots \text{O}23') = 152.7(2)^\circ$] giving rise to a polymeric structure (see Fig. 3).

Compound II. 0.5EtOAc. **II** crystallizes with acetyl acetate. The EtOAc solvent molecules lie on a crystallographic mirror plane perpendicular to the *b* axis. A drawing of **II** is shown in Fig. 4, and selected bond lengths and angles are listed in Table 3. The conformation of the $\text{O}-\text{C}=\text{O}-\text{S}-\text{N}-\text{C}=\text{O}-\text{N}$ skeleton of **II** is nearly the same as the corresponding one of both molecules of **I**. In fact, the *rms* deviations between homologous non-H atoms in the best least-squares structural fitting of the skeletons of **I** and **II** are less than 0.1 \AA . Neighboring molecules in the lattice, symmetry-related by a crystallographic *a*-glide plane perpendicular to the *c* axis, are linked through a bifurcated N–H \cdots O \cdots H–N bond where both N–H groups of a given molecule act as donors and one of the carbonyl oxygen atom (O3) of a neighbor molecule acts as an acceptor [$d(\text{N}1 \cdots \text{O}3') = 2.827(3) \text{ \AA}$, $\angle(\text{N}1-\text{H}1 \cdots \text{O}3') = 154.8(2)^\circ$ and

Table 1
Assignment of the characteristic vibrational modes of the main $-\text{C}(\text{O})\text{SN}(\text{H})\text{C}(\text{O})\text{N}-$ moiety contained in **I** and **II** compounds.

Experimental		Raman ^a		Calculated ^b		Assignment/symmetry
I	II	I	II	I	II	
	3359s				3616 (23)	$\nu(\text{N}-\text{H})$ [C–N–C]/A
3274s	3250s			3628 (23)	3581 (21)	$\nu(\text{N}-\text{H})$ [S–N–C]/A
1735vs	1741vs	1729m	1726m	1788 (230)	1794 (194)	$\nu(\text{C}=\text{O})$ [O–C–S]/A
1698	1694					$\nu(\text{C}=\text{O})^{**}$
1655vs	1659vs	1648w	1658m	1743 (388)	1772 (290)	$\nu(\text{C}=\text{O})$ [N–C–N]/A
	1546s				1534 (240)	$\rho(\text{N}-\text{H})$ [C–N–C]/A
1474s	1470m	1460m	1466s	1462 (260)	1494 (75)	$\rho(\text{N}-\text{H})$ [O–N–C]/A
1192s	1156vs	–	1222m	1177 (336)	1200 (120)	$\nu_{\text{as}}(\text{C}-\text{O}-\text{C})/A$
1049w	1040w	1053w	1036w	1152 (473)	1034 (128)	$\nu_{\text{as}}(\text{S}-\text{N}-\text{C})/A$
887vw	877w	886w	878m	873 (4)	867 (15)	$\nu(\text{S}-\text{N})/A$
782vw	740vw	782vw	741w	780 (12)	762 (2)	$\delta_{\text{oop}}(\text{N}-\text{C}(\text{O})\text{N})/A$
675w	647m	–	–	675 (8)	674 (8)	$\delta_{\text{oop}}(\text{O}-\text{C}(\text{O})\text{S})/A$

^a Band intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

^b In parentheses: calculated relative values for the more stable conformers, IR intensities of compound **I**, 100% \equiv 473.42 Km/mol, and compound **II**, 100% \equiv 708.23 Km/mol.

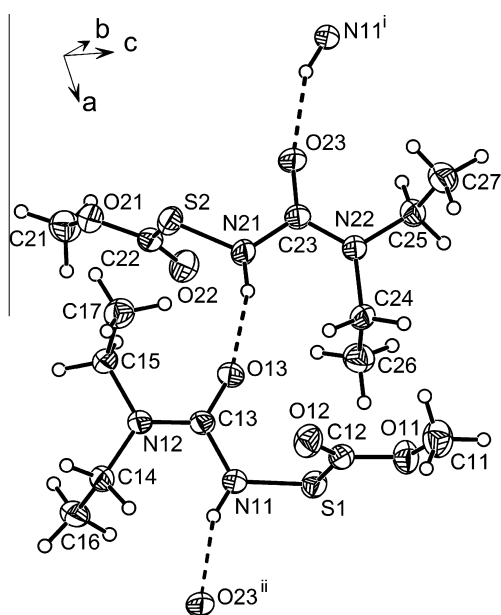


Fig. 3. ORTEP [18] of a dimer in the asymmetric unit of **I** showing the labeling of the non-H atoms and their displacement ellipsoids at the 30% probability level. The H atoms are shown as spheres with arbitrary radius. The intra- and inter-dimer N–H...O bonds are indicated by dashed lines. Neighboring dimers are obtained through the symmetry operations (i) $x-1, y+1, z$; (ii) $x+1, y-1, z$.

Table 2
Selected bond lengths (Å) and angles (°) in **I**.

C(11)–O(11)	1.441(3)	C(12)–O(12)	1.187(2)
C(12)–O(11)	1.334(2)	C(12)–S(1)	1.773(2)
C(13)–O(13)	1.229(2)	C(13)–N(12)	1.339(2)
C(13)–N(11)	1.395(2)	C(14)–N(12)	1.464(2)
C(14)–C(16)	1.505(3)	C(15)–N(12)	1.465(2)
C(15)–C(17)	1.501(3)	N(11)–S(1)	1.663(2)
C(21)–O(21)	1.444(2)	C(22)–O(22)	1.193(2)
C(22)–O(21)	1.334(2)	C(22)–S(2)	1.771(2)
C(23)–O(23)	1.226(2)	C(23)–N(22)	1.344(2)
C(23)–N(21)	1.395(2)	C(24)–N(22)	1.469(2)
C(24)–C(26)	1.507(3)	C(25)–N(22)	1.468(2)
C(25)–C(27)	1.500(3)	N(21)–S(2)	1.660(2)
O(12)–C(12)–O(11)	126.6(2)	O(12)–C(12)–S(1)	125.7(2)
O(11)–C(12)–S(1)	107.7(1)	O(13)–C(13)–N(12)	122.9(2)
O(13)–C(13)–N(11)	120.0(2)	N(12)–C(13)–N(11)	117.1(1)
N(12)–C(14)–C(16)	112.7(2)	N(12)–C(15)–C(17)	113.4(2)
C(13)–N(11)–S(1)	120.0(1)	C(13)–N(12)–C(15)	117.4(1)
C(13)–N(12)–C(14)	125.2(1)	C(15)–N(12)–C(14)	117.1(1)
C(12)–O(11)–C(11)	116.4(2)	N(11)–S(1)–C(12)	101.14(8)
O(22)–C(22)–O(21)	126.2(2)	O(22)–C(22)–S(2)	126.6(2)
O(21)–C(22)–S(2)	107.2(1)	O(23)–C(23)–N(22)	123.3(2)
O(23)–C(23)–N(21)	120.2(2)	N(22)–C(23)–N(21)	116.4(2)
N(22)–C(24)–C(26)	112.3(2)	N(22)–C(25)–C(27)	112.1(2)
C(23)–N(21)–S(2)	120.8(1)	C(23)–N(22)–C(25)	118.3(2)
C(23)–N(22)–C(24)	125.1(2)	C(25)–N(22)–C(24)	116.3(1)
C(22)–O(21)–C(21)	116.7(2)	N(21)–S(2)–C(22)	101.60(9)

$d(\text{N2} \cdots \text{O3}') = 3.066(3) \text{ \AA}$, $\angle(\text{N2}–\text{H2} \cdots \text{O3}') = 149.8 (2)^\circ$. This hydrogen bonding gives rise to a polymeric chain along the *a*-axis (see Fig. 4).

3. Conclusion

Two *N*'-methoxycarbonylsulfonyl-substituted ureas were prepared in high yield and purity by treating $\text{CH}_3\text{OC(O)SNO}$ with the corresponding amines at room temperature. Conformational and structural properties were determined by using experimental tech-

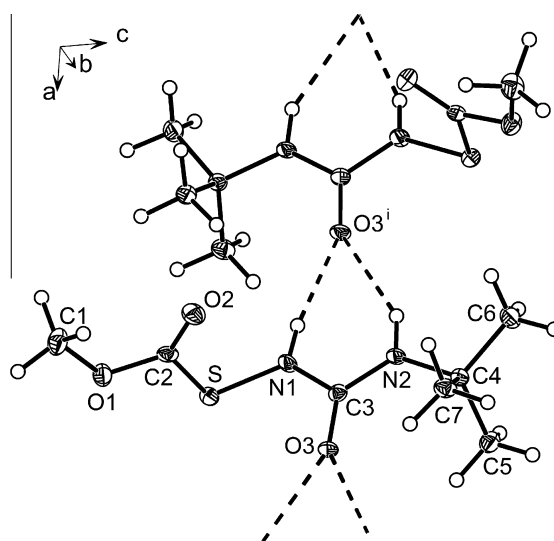


Fig. 4. Drawing of two neighboring hydrogen-bonded molecules in the **II** 1/2EtOAc crystal. The displacement ellipsoids of the non-H atoms are drawn at the 30% probability level. The upper molecule is obtained from the bottom one through the symmetry operation (i) $x-1/2, y, -z+3/2$. For clarity, the EtOAc molecule is not included in the figure.

Table 3
Selected bond lengths (Å) and angles (°) of **II** molecule in **II** 1/2EtOAc.

S–N(1)	1.655(2)
S–C(2)	1.775(3)
O(1)–C(2)	1.330(3)
O(1)–C(1)	1.451(3)
O(2)–C(2)	1.190(3)
O(3)–C(3)	1.240(2)
N(1)–C(3)	1.378(3)
N(2)–C(3)	1.336(3)
N(2)–C(4)	1.479(3)
C(4)–C(7)	1.519(3)
C(4)–C(6)	1.526(3)
C(4)–C(5)	1.526(3)
N(1)–S–C(2)	100.6(1)
C(2)–O(1)–C(1)	116.0(2)
C(3)–N(1)–S	122.2(2)
C(3)–N(2)–C(4)	126.1(2)
O(2)–C(2)–O(1)	126.7(2)
O(2)–C(2)–S	126.0(2)
O(1)–C(2)–S	107.3(2)
O(3)–C(3)–N(2)	124.9(2)
O(3)–C(3)–N(1)	120.9(2)
N(2)–C(3)–N(1)	114.2(2)
N(2)–C(4)–C(7)	110.2(2)
N(2)–C(4)–C(6)	106.2(2)
C(7)–C(4)–C(6)	109.3(2)
N(2)–C(4)–C(5)	110.2(2)
C(7)–C(4)–C(5)	111.3(2)
C(6)–C(4)–C(5)	109.4(2)

niques which include vibrational spectroscopy (IR and Raman) as well as X-ray diffraction analysis. For both substances, it was determined that the molecular skeleton is essentially planar. N–H...O=C intermolecular hydrogen bonds dictate the crystal structure. Bifurcated N–H...O...H–N bonds are present in **II**, where both N–H groups of a given molecule act as donors and one of the carbonyl oxygen atom (O3) of a neighbor molecule acts as an acceptor. These interactions have strong effects on the vibrational properties, where low frequency values for the $\nu(\text{C}=\text{O})$ stretching mode of the urea moiety in the IR spectra of the compounds were observed.

4. Experimental

4.1. Synthesis

N,N-Diethyl-*N'*-methoxycarbonylsulfenyl urea (**I**) and *N*-*tert*-butyl-*N'*-methoxycarbonylsulfenyl urea (**II**) were synthesized by nucleophilic addition of the respective amines to $\text{CH}_3\text{OC}(\text{O})\text{SNCO}$ as reported recently [10]. Thus, freshly distilled $\text{CH}_3\text{OC}(\text{O})\text{SNCO}$ (1 g, 7.52 mmol) was kept in a Carius tube closed by a Young valve or in a Schlenk tube (under nitrogen or argon atmosphere) at -65°C in a liquid nitrogen/ethanol bath. An excess of the corresponding diethyl or *tert*-butyl amine (8.30 mmol) was condensed into the tube. The reaction mixture was kept without stirring for 30 min at low temperature, then for 15 min at -40°C with temporary shaking and finally left for 15 min at room temperature. After removing the excess of the respective amine, the remaining pale yellow solids were purified by re-crystallization from EtOAc/toluene (2:1 v/v) (for **I**) and EtOAc (for **II**) and obtained as clear white plates (**I**) and needles (**II**). The purity of the final compounds was controlled by ^1H NMR spectroscopy.

4.2. Characterization

N,N-Diethyl-*N'*-methoxycarbonylsulfenyl urea (**I**). Yield (1.24 g, 80%); Melting point (not corrected) $76(1)^\circ\text{C}$; GC chromatogram (EtOAc) shows a single peak at a retention time of 7.29 min; GC-MS (EI, 70 eV) m/z [relative intensity, fragment]; 206 [<2 , M^+], 133 [35, $\text{CH}_3\text{OC}(\text{O})\text{SNC}(\text{O})^+$], 100 [40, $(\text{C}_2\text{H}_5)_2\text{NC}(\text{O})^+$], 72 [50, $(\text{C}_2\text{H}_5)_2\text{N}^+$], 59 [90, $\text{CH}_3\text{OC}(\text{O})^+$], 58 [100, $(\text{C}_2\text{H}_5)_2^+$], 15 [60, CH_3^+]. ^1H NMR (CDCl_3) δ 6.34 (s, 1H, NH), 3.78 (s, 3H, CH_3O), 3.31 (q, $^3J_{\text{HH}} = 7.2$ Hz, 4H, $-\text{CH}_2-$), 1.13 ppm (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, $-\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 173.0 (S=C=O), 156.1 (N=C=O), 54.6 (CH_3O), 42.4 (CH_2), 13.9 ppm (CH_3).

N-*tert*-Butyl-*N'*-methoxycarbonylsulfenyl urea (**II**). Yield (1.32 g, 85%); Melting point (not corrected) $119(1)^\circ\text{C}$; GC chromatogram (CHCl_3) shows a single peak at a retention time of 12.20 min; GC-MS (EI, 70 eV) m/z [relative intensity, fragments]; 206 [<1 , M^+], 191 [1, $\text{CH}_3\text{OC}(\text{O})\text{SN}(\text{H})\text{C}(\text{O})\text{N}(\text{H})\text{C}(\text{CH}_3)_2^+$], 107 [100, $\text{CH}_3\text{OC}(\text{O})\text{SNH}_2^+$], 59 [12, $\text{CH}_3\text{OC}(\text{O})^+$], 57 [55, $\text{C}(\text{CH}_3)_3^+$], 41 [12, C_3H_5^+], 15 [4, CH_3^+]. ^1H NMR (CDCl_3) δ 5.70 (s, 1H, S-NH), 5.39 (s, 1H, NHBU^t), 3.89 (s, 3H, OCH_3), 1.36 ppm (s, 9H, $\text{C}(\text{CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 171.5 (S=C=O), 155.5 (N=C=O), 54.8 (CH_3O), 51.2 ($\text{C}(\text{CH}_3)_3$), 29.8 ppm ($\text{C}(\text{CH}_3)_3$).

4.3. Instrumentation

4.3.1. X-ray diffraction data

The measurements were performed on an Oxford Xcalibur, Eos, Gemini CCD diffractometer with graphite-monochromated $\text{Cu K}\alpha$ ($\lambda = 1.54184 \text{ \AA}$) radiation for compound **I** and $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation for **II**. X-ray diffraction intensities were collected (ω scans with θ and κ -offsets), integrated and scaled with CrysAlisPro [18] suite of programs. The unit-cell parameters were obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro. Data were corrected empirically for absorption employing the multi-scan method implemented in CrysAlisPro. The structures were solved by direct methods with SHELXS-97 [18] and the molecular model refined by full-matrix least-squares procedure with SHELXL-97 [18].

The hydrogen atoms were positioned stereo-chemically and refined with the riding model. The locations of all methyl hydrogen atoms but the ones of the methyl groups of the EtOAc in **II**.05EtOAc were refined by treating them as rigid bodies which were allowed to rotate around the corresponding C- CH_3 and

Table 4
Crystal data and structural refinement results for compounds **I** and **II** 1/2EtOAc.

	Compound I	Compound II 1/2EtOAc
Empirical formula	$\text{C}_7\text{H}_{14}\text{N}_2\text{O}_3\text{S}$	$\text{C}_9\text{H}_{18}\text{N}_2\text{O}_4\text{S}$
Formula weight	206.26	250.31
Temperature (K)	294(2)	130(2)
Wavelength (\AA)	1.54184	0.71069
Crystal system, space group	Triclinic, $P-1$ (#2)	Orthorhombic, Pnma (#62)
Unit cell dimensions		
a (\AA)	7.9471(4)	9.365(5)
b (\AA)	8.6672(4)	26.577(5)
c (\AA)	16.0447(8)	10.287(5)
α ($^\circ$)	80.335(4)	90.00
β ($^\circ$)	87.087(4)	90.00
γ ($^\circ$)	75.271(4)	90.00
Volume (\AA^3)	1053.62(9)	2560(2)
Z , calculated density (Mg/m^3)	4, 1.300	8, 1.299
Absorption coefficient (mm^{-1})	2.607	0.255
$F(000)$	440	1072
Crystal size (mm)	$0.26 \times 0.20 \times 0.05$	$0.80 \times 0.02 \times 0.02$
Crystal color/shape	Colorless/plate	Colorless/needle
θ -range for data collection ($^\circ$)	5.35–74.05	2.94–26.00
Index ranges	$-9 \leq h \leq 9$, $-10 \leq k \leq 9$, $-19 \leq l \leq 19$	$-11 \leq h \leq 11$, $-27 \leq k \leq 32$, $-12 \leq l \leq 11$
Reflections collected/unique	9939/4253 [$R(\text{int}) = 0.0259$]	21584/2566 [$R(\text{int}) = 0.0859$]
Completeness (%)	99.6 (to $\theta = 74.05^\circ$)	99.9 (to $\theta = 26.00^\circ$)
Observed reflections [$I > 2\sigma(I)$]	3377	1614
Max. and min. transmission	1.0 and 0.5591	1.0 and 0.8898
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Weights, w	$[\sigma^2(F_o^2) + (0.076P)^2]^{-1}$ $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$	$[\sigma^2(F_o^2) + (0.038P)^2]^{-1}$ $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$
Data/restraints/parameters	4253/0/241	2566/0/159
Goodness-of-fit on F^2	1.030	0.965
Final R indices ^a [$I > 2\sigma(I)$]	$R1 = 0.0410$, $wR2 = 0.1111$	$R1 = 0.0441$, $wR2 = 0.0773$
R indices (all data)	$R1 = 0.0498$, $wR2 = 0.1154$	$R1 = 0.0983$, $wR2 = 0.0889$
Largest peak and hole (e \AA^{-3})	0.247 and -0.480	0.257 and -0.231

^a R indices defined as: $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

O—CH₃ bonds to maximize the sum of the observed electron density at the calculated H-positions. As a result, these CH₃ groups converged to staggered conformations. The H atoms of the O—CH₃ groups showed positional disorder which could be modeled as two split —CH₃ orientations compatible with the crystallographic *m* symmetry site occupied by the EtOAc solvent molecule. Crystal data and details of structure refinements are summarized in Table 4. Crystallographic structural data have been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC 901395 (I) and CCDC 9 96 (II·0.5EtOAc) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.3.2. NMR spectroscopy

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded in CDCl₃ on a Bruker AVANCE-DRX-400 instrument. Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a Bruker AC 400 (100.61 MHz).

4.3.3. Vibrational spectroscopy

Infrared spectra were recorded as KBr pellets in the 4000–400 cm⁻¹ range on a Perkin-Elmer System 2000 FTIR spectrometer and on a Bruker EQUINOX 55 FTIR spectrometer. FT-Raman spectra of solid samples were run with a Bruker 66 with FRA 106 Raman accessory, excited with 100 mW of a 1064 nm Nd:YAG laser.

4.3.4. GC-MS Determination

The GC-MS measurements were recorded with a GCMS-QP2010 SHIMADZU instrument using gaseous helium as mobile phase with the pressure in the column head equal to 100 kPa. The column used was a 19091 J-433 HP-5 (30 × 0.32 × 0.25 mm). Approximately 1 μL volume of the compounds dissolved in CHCl₃ and C₂H₅OC(O)CH₃ were chromatographed using the following general conditions: the injection temperature was 200 °C, the initial column temperature (70 °C) was kept for 2 min, then the temperature was increased to 200 °C (heating rate of 10 °C/min) and maintained at this temperature for 4 min. This was followed by a final heating to 250 °C (10 °C/min) after which the column was kept at this temperature for further 2 min. The spectrometer source temperature was maintained at 200 °C.

4.3.5. Melting point determination

The melting points were determined in a capillary tube containing the pulverized sample, which was introduced in a BÜCHI melting point apparatus equipped with a thermometer (0–300(1) °C).

4.3.6. Theoretical calculations

All quantum chemical calculations were performed with the GAUSSIAN 03 program package [19]. The molecular geometries were optimized to standard convergence criteria by using a DFT hybrid method with Becke's non-local three-parameter exchange interaction and the Lee, Young and Parr correction (B3LYP) using 6-31G* and 6-311++G** basis sets. Table S11 lists selected experi-

mental and computed (B3LYP/6-311++G**) geometric parameters for compounds I and II.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2012.12.047>.

References

- [1] T. Theophanides, P.D. Harvey, *Coord. Chem. Rev.* 76 (1987) 237.
- [2] B. Rousseau, C. Van Alsenoy, R. Keuleers, H.O. Desseyn, *J. Phys. Chem. A* 102 (1998) 6540.
- [3] A. Masunov, J.J. Dannenberg, *J. Phys. Chem. A* 103 (1999) 178.
- [4] R.W. Gora, W. Bartkowiak, S. Roszak, J. Leszczynski, *J. Chem. Phys.* 117 (2002) 1031.
- [5] R.G. Arnold, J.A. Nelson, J.J. Verbanc, *Chem. Rev.* 57 (1957) 47.
- [6] W. Kolodziejski, I. Wawer, K. Wozniak, J. Klinowski, *J. Phys. Chem. A* 97 (1993) 12147.
- [7] A. Haas, H. Reinke, *Chem. Ber.* 102 (1969) 2718.
- [8] S. Torrico-Vallejos, M.F. Erben, R. Boese, O.E. Piro, E.E. Castellano, C.O. Della Védova, *J. Mol. Struct.* 918 (2009) 146.
- [9] S. Torrico-Vallejos, M.F. Erben, H. Willner, R. Boese, C.O. Della Védova, *J. Org. Chem.* 72 (2007) 9074.
- [10] S. Torrico-Vallejos, M.F. Erben, E. Hey-Hawkins, C.O. Della Védova, *Tetrahedron Lett.* 52 (2011) 5352.
- [11] M.F. Erben, C.O. Della Védova, R.M. Romano, R. Boese, H. Oberhammer, H. Willner, O. Sala, *Inorg. Chem.* 41 (2002) 1064.
- [12] S. Torrico-Vallejos, M.F. Erben, M.-F. Ge, H. Willner, C.O. Della Védova, *J. Phys. Chem. A* 114 (2010) 3703.
- [13] S. Torrico-Vallejos, M.F. Erben, O.E. Piro, E.E. Castellano, C.O. Della Védova, *Polyhedron* 28 (2009) 937.
- [14] K. Srinivasan, S. Gunasekaran, S. Krishnan, *Spectrochim. Acta* 75A (2010) 1171.
- [15] Y. Mido, I. Kitagawa, M. Hashimoto, H. Matsuura, *Spectrochim. Acta* 55A (1999) 2623.
- [16] A. Saeed, M.F. Erben, U. Flörke, *J. Mol. Struct.* 982 (2010) 91.
- [17] A. Saeed, M.F. Erben, U. Shaheen, U. Flörke, *J. Mol. Struct.* 1000 (2011) 49.
- [18] E.R. Andrew, D. Hyndman, *Discuss. Faraday Soc.* 19 (1955) 195.
- [19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc.: Pittsburgh PA, 2003.