# Preparation and Properties of Methoxycarbonylsulfenyl Isocyanate, $CH_3OC(O)SNCO$

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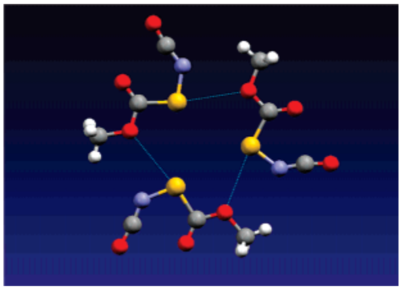

Pure methoxycarbonylsulfenyl isocyanate, $CH_3OC(O)SNCO$, is quantitatively prepared by the metathesis reaction between $CH_3OC(O)SCl$ and AgNCO. This novel species has been obtained in its pure form and characterized by $^1H$ and $^{13}C$ NMR, UV−vis, FTIR, and FT-Raman spectroscopy. The conformational properties of the gaseous molecule have been studied by vibrational spectroscopy and quantum chemical calculations (B3LYP and MP2 methods). The compound exhibits a conformational equilibrium at room temperature having the most stable form $C_S$ symmetry with the C═O double bond synperiplanar with respect to the S−N single bond. A second form was observed in the IR spectrum and corresponds to a conformer possessing the C−S bond antiperiplanar with respect to the N═C double bond of the isocyanate group. The structure of a single crystal of $CH_3OC(O)SNCO$ was determined by X-ray diffraction analysis at low temperature using a miniature zone melting procedure. The crystalline solid (triclinic, $P\bar{1}$, $a$ = 8.292(6) Å, $b$ = 9.839(7) Å, $c$ = 11.865(8) Å, $\alpha$ = 67.290(2)°, $\beta$ = 71.5570(10)°, $\gamma$ = 83.4850(10)° and $Z$ = 6) shows the presence of molecules having exclusively a synperiplanar conformation with respect to the three $\phi$(CO−C═O), $\phi$(O═C−SN), and $\phi$(CS−N═C) dihedral angles.

## Introduction

Isocyanate species are of great chemical interest because the −N═C═O group is of fundamental importance in the formation of polyurethane polymers, which offer interesting possibilities for a variety of important technological applications.[1] The very first isocyanate molecule of the type RSNCO; with the isocyanate group attached directly to a divalent sulfur atom is known since 1963, when Emeléus and Haas synthesized $CF_3SNCO$.[2] A few other species such as XC(O)SNCO (X = F, Cl) were also synthesized.[2b] Very recently, Maofa Ge et al.[3] have reported a photoelectron spectroscopy study on the sulfur-containing diisocyanates $S(NCO)_2$ and $OS(NCO)_2$. Interesting, because the hypothiocyanate anion has been reported to have significant antimicrobial properties, HSNCO and the related anions have

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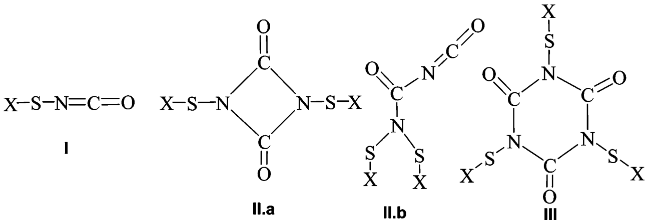
been studied by means of ab initio calculations and experimental techniques. These studies revealed the linear $[SNCO]^-$ structure as the most stable isomer in the electronic ground state.[4]

The conformational stability of simple isocyanates has been difficult to predict and may also be different in different aggregation states. For example, in acetyl isocyanate, $CH_3C(O)NCO$,[5] the main conformation changes from the gas to the liquid phase. Furthermore, the conformational stability of the XC(O)NCO (X = F,[6,7] Cl,[8−11] Br,[12] $CH_3$,[13−15] and $CF_3$[16]) molecules in the vapor state depends on the X substituent. Some controversies have been also reported between the experimental and the calculated conformational properties of simple isocyanates challenging the reliability of ab initio calculations. For instance, while vibrational spectra[9,10] and gas electron diffraction studies[11] are consistent with the preference of the anti form (isocyanate group anti with respect to the C═O double bond) of ClC(O)NCO in both the gas and liquid phases, most ab initio calculations predict the syn form as the most stable conformer.[11,17−19] The information about the molecular structure and conformational properties of RSNCO species is still scarce. The gas-phase molecular structure of FC(O)SNCO has been studied by using the gas electron diffraction technique complemented with quantum chemical calculations.[20] A slightly nonplanar structure with a $\phi$(CS−N═C) torsional angle around the S−N single bond of 17(6)° was observed. A vibrational study which included matrix isolated and gas-phase FTIR spectroscopy supports the presence of a unique conformation at room temperature.[21]

It is well-known that phenyl isocyanate gives a cyclic dimer (1,3-diphenyl-2,4-uretidinedione) in the presence of tertiary amines as catalyst.[22−24] Similarly, FC(O)SNCO also yields a FC(O)S−substituted uretidinedione.[25] However, $CF_3SNCO$ dimerizes to *N,N*-bis(trifluoromethanesulfenyl)carbamoyl isocyanate, $(CF_3S)_2NC(O)NCO$, as confirmed by spectroscopic and chemical evidence.[2] Furthermore $CF_3SNCO$ trimerizes at 100 °C to tris(trifluoromethanesulfenyl) isocyanurate.[2] Thus, very rich chemical and structural features are anticipated for sulfenyl isocyanate especies (Scheme 1). Moreover, very recently, $CH_3NCO$ and its cyclic oligomers $(CH_3NCO)_n$ ($n$ = 2, 3, 4) have been computed. The cyclic trimer, as expected, was found to be more stable than the dimer and the tetramer.[26]

**SCHEME 1. Representation of the Monomeric Sulfenyl Isocyanate Molecule (I), the Cyclic Dimer (1,3-Sulfenyl-2,4-uretidinedione) (II.a), the Dimeric Species *N,N*-Bis(sulfenyl)carbamoyl Isocyanate (II.b) and the Trimeric Tris(sulfenyl) Isocyanurate Specie (III)**



Herein the preparation and characterization of a novel RSNCO compound, methoxycarbonylsulfenyl isocynate, $CH_3OC(O)SNCO$ are presented. In this study we undertake an experimental investigation of the structure and vibrational properties of the title compound, which includes the use of vibrational [IR (gas) and Raman (liquid)] and NMR ($^1$H and $^{13}$C) spectroscopies. The crystal structure of the compound was also determined at 203 K by X-ray diffraction using an in situ crystallization method. The experimental data were supplemented by using ab initio (HF and MP2) and DFT (B3LYP) quantum chemical calculations.

## Results

**Synthesis.** Silver isocyanate and carbonylsulfenyl chlorides XC(O)SCl (X = F, Cl) are ideal precursors for the preparation of monomeric XC(O)SNCO (X = F, Cl) species.[25] Thus, $CH_3OC(O)SNCO$ was synthesized quantitatively by reacting methoxycarbonylsulfenyl chloride, $CH_3OC(O)SCl$, with silver isocyanate for 2 h at room temperature. The final purity was checked by IR (Figure 1) and $^1$H NMR spectroscopy. No evidence was found for the formation of dimeric or higher polymeric species.

**Quantum Chemical Calculations.** Several conformations of $CH_3OC(O)SNCO$ are feasible, depending on the orientation around the O−C, C−S, and S−N single bonds. The molecular structure and conformational properties for the related $CH_3OC(O)SCl$ and FC(O)SNCO species have been studied in both gaseous and solid phases.[27,20]According to these antecedents, a

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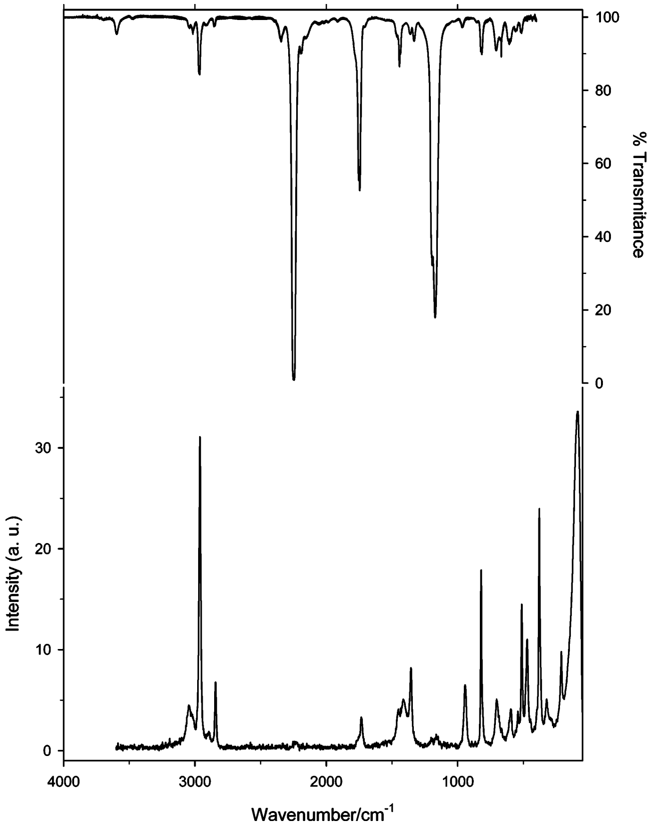

**FIGURE 1.** Gas IR at 1.7 mbar (glass cell, 200 mm optical path length, Si windors, 0.5 mm tick) and liquid Raman spectra for CH$_3$OC(O)-SNCO.

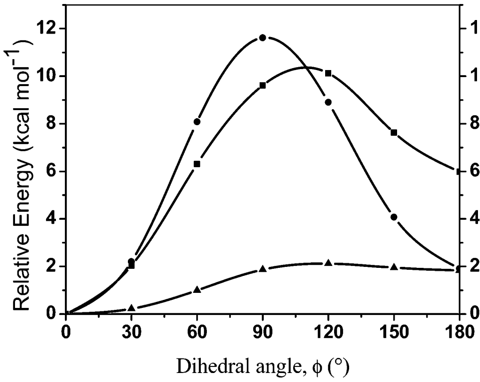

**FIGURE 2.** Calculated (B3LYP/6-31G*) potential function for internal rotation around the O$-$C (-■-), C$-$S (-●-) and S$-$N (-▲-) single bonds in CH$_3$OC(O)SNCO.

structure for the title compound with whole synperiplanar orientation around the O$-$C, C$-$S, and S$-$N single bonds was used as the initial form in the calculations. To gain insights in the conformational preference of the title molecule, the potential energy functions for internal rotation around the $\phi$(CO$-$C$=$O), $\phi$(O$=$C$-$SN), and $\phi$(CS$-$N$=$C) dihedral angles were calculated at the B3LYP/6-31G* level, by allowing geometry optimizations with the respective dihedral angles ($\phi$) varying from 0° (syn position) to 180° (anti position) in steps of 30°. The potential energy curves are shown in Figure 2.

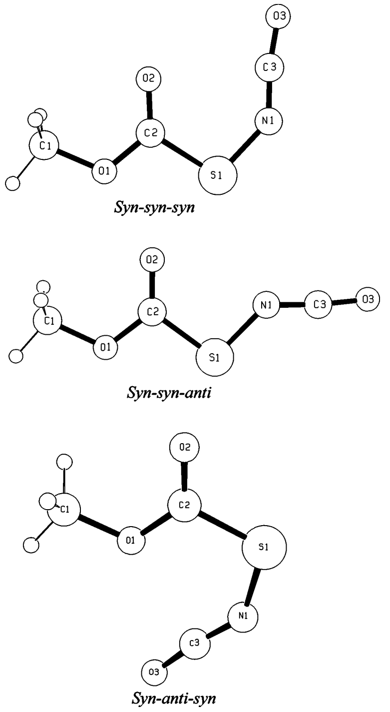

**FIGURE 3.** Molecular models with atom numbering scheme for the syn$-$syn$-$syn, syn$-$syn$-$anti, and syn$-$anti$-$syn conformers of CH$_3$-OC(O)SNCO.

As expected for the methoxycarbonyl CH$_3$OC(O)$-$ moiety,[27,30−34] a syn orientation of the $\phi$(CO$-$C$=$O) dihedral angle is preferred, being the anti form higher in energy. Likewise, two structures correspond to minima in the potential energy curve around the $\phi$(O$=$C$-$SN) dihedral angle. The most stable one shows syn orientation of the C$=$O and S$-$N bonds while the anti form is located higher in energy by ca. 1.9 kcal mol$^{-1}$. Similarly, the resulting potential energy curve for the rotation of the $\phi$(CS$-$N$=$C) dihedral angle possesses minima for two planar forms; the syn form is ca. 1.8 kcal mol$^{-1}$ more stable than the anti conformer.

Moreover, full geometry optimizations and frequency calculations were performed for each of the most stable structures at higher levels of theoretical approximations which include HF and B3LYP methods with the 6-31G* and the more extended 6-311++G** basis sets. Relative $\Delta E°$ energy values (corrected by zero-point energy) are listed in Table S1 (Supporting Information). All computational methods predict a structure with syn orientation around the three dihedral angles, (syn$-$syn$-$syn form in Figure 3) to be the most stable conformer of CH$_3$-OC(O)SNCO. The second stable form, higher in energy by 1.10 kcal mol$^{-1}$ (B3LYP/6-311++G**) corresponds to a conformer with anti orientation of the $\phi$(CS$-$N$=$C) dihedral angle (syn$-$

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**TABLE 1. Selected Experimental and Calculated Geometric Parameters for the Syn−Syn−Syn Conformer of $CH_3OC(O)SNCO$ and Experimental Values[20] for the Gas-Phase Structure of FC(O)SNCO**

| parameters[a] | X-ray[b] | B3LYP 6-311++G** | MP2 6-31G* | FC(O)SNCO[20] |
|---|---|---|---|---|
| S−N | 1.665 (2) | 1.683 | 1.686 | 1.669 (3) |
| S−C2 | 1.771 (2) | 1.803 | 1.783 | 1.748 (5) |
| N═C | 1.195 (3) | 1.214 | 1.232 | 1.208 (8) |
| O2═C2 | 1.196 (2) | 1.200 | 1.215 | 1.187 (5) |
| C3═O3 | 1.165 (2) | 1.166 | 1.184 | 1.167 (5) |
| C2−S−N | 100.5 (9) | 101.0 | 100.4 | 101.6 (20) |
| S−N═C | 132.50 (15) | 136.9 | 132.9 | 127.8 (14) |
| O2═C2−S | 124.15 (15) | 124.7 | 125.3 | 129.5 (8) |
| N═C═O | 171.1 (2) | 171.2 | 169.5 | 165.9 (32) |
| $\phi$(CS−N═C) | −2.4 (2) | 0.0 | 0.0 | 17 (6) |
| $\phi$(C═O−SN) | 1.6 (2) | 0.0 | 0.0 | 0.0 (not refined) |
| $\phi$(SN−C═O) | 180.00 (10) | 180.0 | 180.0 | |

[a] For atom numbering see Figure 3. [b] Average values from the three nonequivalent form of the molecule in the cystal.

syn−anti form in Figure 3). A third conformer named syn−anti−syn in Figure 3, with anti orientation of the C═O and S−N bonds results to be minima in the potential hypersurface as well, located at 1.33 kcal $mol^{-1}$ above the global minimum. Not surprisingly, HF method predicts the anti form around to the S−N single bond as a transition state, with one imaginary frequency of vibration. A similar result was reported for the FSNCO molecule at these levels of calculations.[21] Other forms (see Table S1) were found to be stable conformers of $CH_3OC(O)SNCO$, with calculated energies higher than 2 kcal $mol^{-1}$ with respect to the minimum and are not expected to be clearly detected under the conditions used in our experiments.

Selected geometric parameters calculated for the most stable conformer (B3LYP/6-311++G**) are listed in Table 1. To include explicitly the electronic correlation in the geometry optimization, MP2/6-31G* calculations were carried out for the most stable *syn−syn-syn* form; these results are also shown in Table 1.

**Vibrational Analysis.** The IR (gas) and Raman (liquid) spectra of $CH_3OC(O)SNCO$ are shown in Figure 1. Experimental and calculated [B3LYP/6-311++G**] frequencies and intensities are given as Supporting Information (Table S2). A tentative assignment of the observed bands was carried out by comparison with spectra of related molecules, specially XC(O)SNCO (X = Cl, F),[3,21] $CH_3OC(O)NCO$,[12] and $CH_3OC(O)SCl$.[27] Moreover, the potential energy distribution (P.E.D.) associated with each normal vibrational mode under the harmonic assumption was also calculated. The symmetry of the title molecule is $C_S$ for any of its possible planar forms. Thus, the $3N - 6 = 27$ normal modes of vibration correspond to an irreducible representation $18A' + 9A''$ for the in-plane and out-of-plane modes, respectively. All vibrations are both infrared and Raman active modes.

The general features of the vibrational spectra of $CH_3OC(O)SNCO$ is dominated by the more stable syn−syn−syn conformer. In view of the rich conformational behavior envisaged by the quantum chemical calculations, a quite detailed analysis of the vibrational spectra has been carried out to assess the presence of more than one conformer of $CH_3OC(O)SNCO$ in the gaseous phase. Thus, the most intense gas-phase IR band at 2248 $cm^{-1}$ was assigned to the N═C═O antisymmetric stretching mode, which appears as a weak signal in the Raman spectrum. On the other hand, the corresponding symmetric motion leads to a rather weak IR absorption but its counterpart at 1350 $cm^{-1}$ is very intense in the Raman spectrum, in agreement with the reported feature in the vibrational spectra of the related isocyanate species.[35,36] The C−S stretch can be assigned with confidence to a moderately intense Raman feature at 511 $cm^{-1}$ (513 $cm^{-1}$ in the IR).

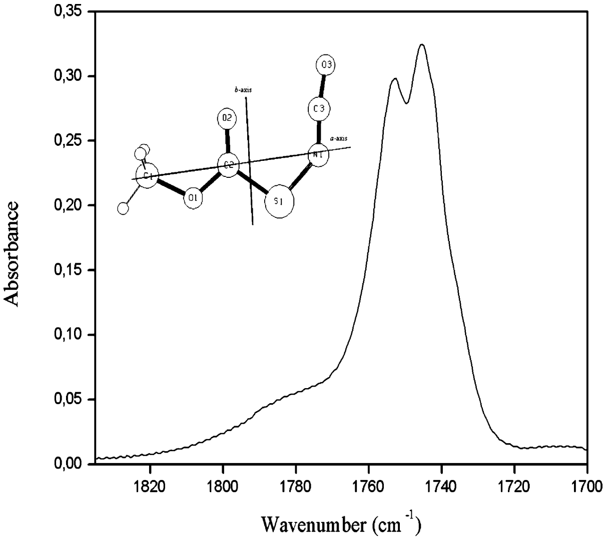

**FIGURE 4.** C═O vibrational stretching region in the IR spectrum of gaseous $CH_3OC(O)SNCO$ at 2 mbar. Principal moments of inertia (*a* and *b*) for the syn−syn−syn conformer of $CH_3OC(O)SNCO$.

Structural changes should affect specific force constants for each conformer, making possible its identification in the vibrational spectra. In particular, it is well-known that the $\nu$(C═O) normal mode of carbonyl compounds is very sensitive to conformational properties.[27,37] For XC(O)NCO (X = F, Cl, $CH_3O$, $CH_3CH_2O$ and $CH_3S$) isocyanates, two bands were observed in the carbonyl stretching region, with clearly defined rotational contours.[12] The carbonyl stretching region of the infrared spectrum of $CH_3OC(O)SNCO$ in the vapor phase is shown in detail in Figure 4, where two absorptions becomes evident at 1750 and 1784 $cm^{-1}$. The well-defined rotational contour of the former band allows assigning this band to the syn−syn−syn form in a straightforward manner. In effect, because of the almost parallel orientation of the carbonyl oscillator with respect to the principal axis of inertia B, a B-type band is expected for the $\nu$(C═O) normal mode of the syn−syn−syn form (see Figure 4). A comparison with the calculated frequencies allows the assignment of the weak absorption at 1784 $cm^{-1}$ to the C═O stretching of the second stable syn−syn−anti conformer of $CH_3OC(O)SNCO$. The calculated wavenumber difference (B3LYP/6-311++G**) for this mode between the two conformers is $-38$ $cm^{-1}$, a value in good agreement with the experimentally observed value in the gas-phase spectrum of $-34$ $cm^{-1}$. For the syn−anti−syn form, a value of 1783 $cm^{-1}$ (B3LYP/6-311++G**) can be computed for this vibration according to our calculations.

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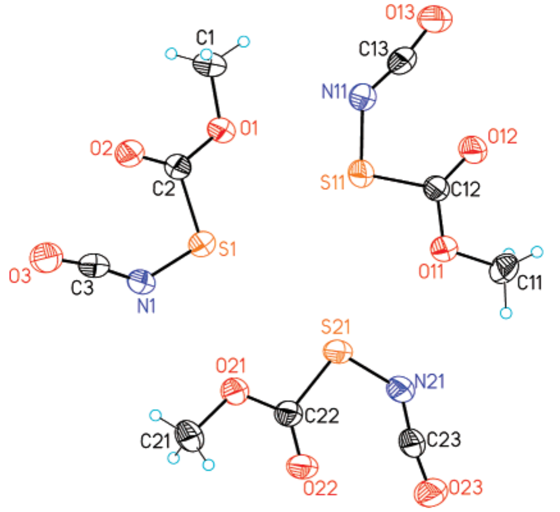

**FIGURE 5.** Stereoscopic illustration of the three crystallographically nonequivalent molecules of $CH_3OC(O)SNCO$ at 203 K.

The conformational equilibrium is also evidenced in the NCO deformation region [$\delta$(NCO), Table S2 in Supporting Information]. From quantum chemical calculations, other fundamental modes in syn−syn−syn and syn−syn−anti conformers differ by less than 2 $cm^{-1}$ and are not expected to be split in either IR (gas) of Raman (liquid) spectra.

**Crystal Structure.** To the best of our knowledge, no reports on crystal structures of molecules containing the −SNCO moiety exist in the literature. This lack of structural data could be related to the fact that simple covalent isocyanate species are liquids or gases at room temperatures and are frequently labile. By using the in-situ crystallization technique,[38] an appropriate single crystal of $CH_3OC(O)SNCO$ was grown at 203 K with a miniature zone melting procedure using focused infrared laser radiation. Methoxycarbonylsulfenyl isocyanate crystallizes in the triclinic $P\bar{1}$ spatial group, with six $CH_3OC(O)SNCO$ molecules in the unit cell ($a = 8.292(6)$, $b = 9.839(7)$ Å, $c = 11.865(8)$ Å, $\alpha = 67.290(2)°$, $\beta = 71.5570(10)°$, $\gamma = 83.4850(10)°$; for whole crystallographic data and refinement information, see Tables S3, S4 and S5 given as Supporting Information). Three crystallographically nonequivalent molecules of $CH_3OC(O)SNCO$ form the unit cell. This cyclic trimeric unit can be seen in Figure 5. Only the most stable syn−syn−syn conformer is observed in a single crystal at 203 K. Each molecule interacts with the other molecules in the trimer unit via the oxygen atom of the methoxy moiety and the sulfur atom with a nonbonded O···S distance of 3.287 Å (average).

The crystal packing of the molecule consists of alternating layers composed by the planar molecules oriented quasi-parallel to the *bc* crystallographic plane (Figure 6). Arranges of trimeric units form the layers, each molecule interacting with another three molecules in the same plane through short contact interactions between the methyl group and the oxygen atoms of both the N═C═O and C═O groups. Intermolecular electrostatic interactions between NCO groups also play a stabilizing role in forming the layer; the averaged nonbonded distance between the oxygen and carbon atoms in NCO groups is 3.119 Å. Two different distances separate the planes; the $C{=}O\cdots CH_3$ intermolecular interaction separates the layers by an amount of 2.696 Å, while the O═C···O═C═N interaction results in a nonbonded distance of 3.217 Å, close to the sum of van der Waals distance for oxygen and carbon atom (3.22 Å). How these nonbonded interactions alternate the molecular layers of crystalline $CH_3OC(O)SNCO$ is illustrated in Figure 7.

Table 1 includes the main geometric parameters derived from the structure refinement. The carbonylsulfenyl isocyanate moiety (−C(O)SNCO) exhibits the following structural parameters: C−S, S−N, and N═C bond lengths are 1.771(2), 1.665(2), and 1.195(3) Å, respectively. The C═O double bond lengths in the sulfenylcarbonyl and the isocyanate groups amount to 1.196(2) and 1.165(2) Å, respectively. The O═C−S, C−S−N, and S−N═C bond angles are 124.15(15)°, 100.5(9)°, and 132.50(15)°, respectively. In Table 1 these parameters are compared with structural data derived from the gas electron diffraction study for the related FC(O)SNCO species.[20] Despite the differences in temperature and technique used in these investigations, the geometrical parameters in the −C(O)SNCO moiety compare fairly well for both species and main deviations are observed in the O═C−S and N═C═O bond angle values. Calculated geometrical parameters (Table 1) reproduce satisfactorily the general molecular dimensions of the crystalline solid. Even with quite large basis sets (6-311++G**) the B3LYP method predicts the S−C bond to be too long by 0.032 Å, while the S−N═C bond angle is calculated 1.7° higher than the experimentally determined value. These parameters are better described by the MP2 method, with differences of only 0.012 Å and 0.4°, respectively.

## Discussion

According to the X-ray diffraction analysis the syn−syn−syn planar structure is present in a single crystal of $CH_3OC(O)SNCO$ at 203 K. The planarity of this molecule can be explained by conjugation between the C═O and N═C═O $\pi$ systems via the p-shaped sulfur lone pairs. However, as has been pointed out for the similar FC(O)SNCO molecule,[20] it would be expected that this structure is destabilized by steric interactions between the N═C═O and C═O groups, with an O2···O3 interatomic contact of 2.59 Å, shorter than the corresponding van der Waals distance of 3.22 Å.[41] Thus, the steric interaction between the C═O and the N═C═O group in the syn−syn−syn conformation of $CH_3OC(O)SNCO$ should lead to an increase in the C−S−N bond angle [100.5 (9)° (X-ray), 101.0° (B3LYP/6-311++G**)]. This increment becomes evident when the value of this bond angle is compared with those calculated (B3LYP/6-311++G**) for the syn−syn−anti conformer for which no such steric repulsion occurs (C−S−N = 97.4°).

The analysis of the vibrational spectra [IR (gas) and Raman (liquid)] of monomeric $CH_3OC(O)SNCO$ agrees with the presence of the syn−syn−syn conformer as the preferred form at room temperature. The contribution of a second form is evidenced in the gaseous infrared spectrum, where two bands are clearly identified in the carbonyl stretching region. The weak band at 1784 $cm^{-1}$ can be assigned with confidence to syn−syn−anti conformer, while the presence of a third syn−anti−

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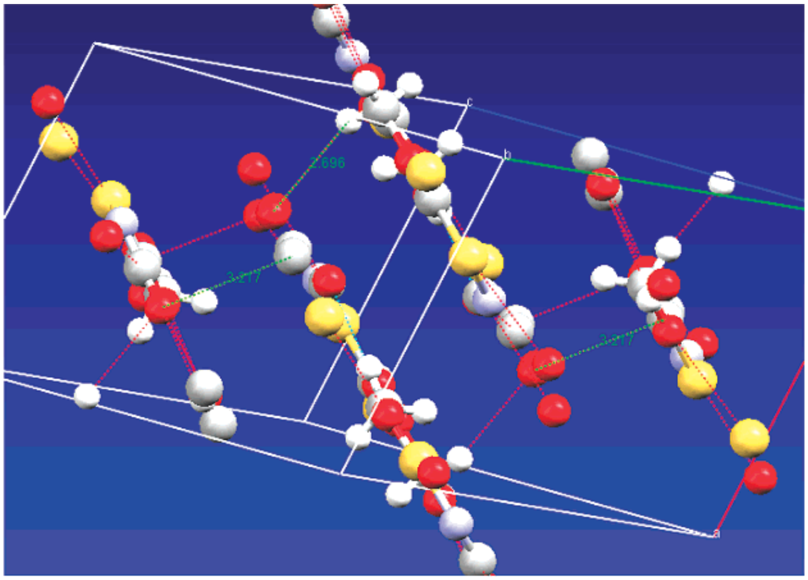

**FIGURE 6.** View of the alternate layers that conform the crystal packing of $CH_3OC(O)SNCO$.

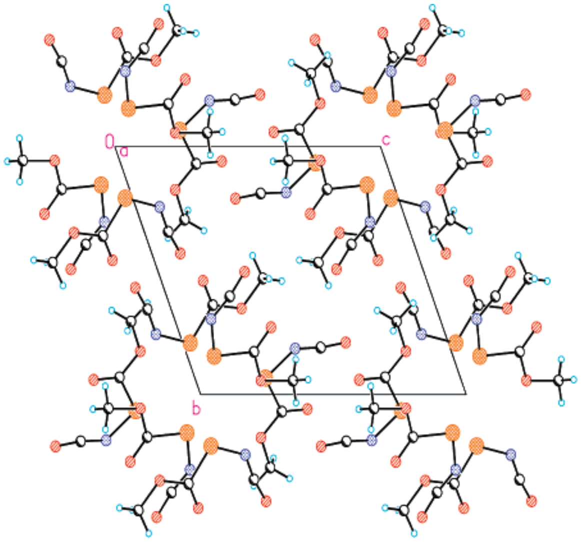

**FIGURE 7.** Packing of molecules in crystalline $CH_3OC(O)SNCO$ at 203 K along the *bc* plane.

syn conformer at ambient temperature cannot be excluded on the basis of the vibrational spectra.

## Experimental Section

**Hazards.** Even if the toxicological activities of $CH_3OC(O)SNCO$ compound have not been investigated, it is known that the high reactivity of isocyanates make them harmful to living tissue. They are toxic and are known to cause asthma in humans, both through inhalation exposure and dermal contact. Exposure to isocyanates and their vapors should be avoided.

**Physical Properties and Spectroscopic Characterization.** The title compound is a colorless liquid, with the characteristic overpowering sulfenylcarbonyl odor. In the liquid or gaseous state, $CH_3OC(O)SNCO$ is stable for several hours at ambient temperature. The white solid sample melts at −57(2) °C. The vapor pressure is 1.7 mbar at 20 °C. The $^1H$ NMR spectrum only shows a singlet located at 3.48 ppm that correspond to the $CH_3O$ group of the molecule. Besides, the $^{13}C$ NMR spectrum shows a quartet signal at 55.7 ppm [$^1J(C,H) = 149.9$ Hz] assigned to the $CH_3$ group, and two singlets at 131.1 and 170.6 ppm, corresponding to the carbon atoms in the NCO and CO groups, respectively. These values are in agreement with reported NMR data for related compounds.[27−29] The UV−vis spectrum of the $CH_3OC(O)SNCO$ vapor shows two bands, one band at $\lambda_{max} = 210$ nm ($\sigma_{max} = 1.34 \times 10^{-21}$ cm$^2$) is assigned to a $\pi \rightarrow \pi^*$ transition of the C=O and N=C=O chromophores.[12] A second, less intense band observed at $\lambda_{max} = 268$ nm ($\sigma_{max} = 2.26 \times 10^{-22}$ cm$^2$), is assigned to the $n \rightarrow \pi^*$ electronic transition related to the O−C(O)S chromophore. Additional evidence for identifying the title compound comes from the analysis of its IR (gas) and Raman (liquid) spectra (Figure 1) and Table S2 (Supporting Information).

**General Procedure and Reagents.** Volatile materials were manipulated in a glass vacuum-line equipped with valves with PTFE stems and a capacitance pressure gauge for the control of the pressure. The pure compound was stored in a flame-sealed glass tubes (6 mm of external diameter) under liquid nitrogen in a long-term Dewar vessel.[42] $CH_3OC(O)SCl$ was purified by fractional trap-to-trap condensation. Finely powdered AgNCO was dried in a vacuum for 4 h at 60 °C before use.

**Instrumentation. (A) X-ray Diffraction at Low Temperature.** An appropriate crystal of ca. 0.3 mm diameter was obtained on the diffractometer at a temperature of 203(2) K with a miniature zone melting procedure using focused-infrared-laser radiation.[38] The diffraction intensities were measured at low temperatures on a four circle diffractometer. Intensities were collected with graphite-monocromatized Mo Kα radiation using the $\omega$-scan technique. The structure was solved by Patterson syntheses and refined by full-matrix least-squares method on $F^2$, with the SHELXTL-Plus program[43] (for further details see the Supporting Information section).

**(B) Vibrational Spectroscopy.** Gas-phase infrared spectra were recorded with a resolution of 1 cm$^{-1}$ in the range 4000−400 cm$^{-1}$. FT-Raman spectra of the liquid substance were run with a resolution of 2 cm$^{-1}$; the sample in a 3 mm glass capillary was excited with 500 mW of a 1064 nm Nd:YAG laser.

**(C) NMR Spectroscopy.** For the $^1H$ and $^{13}C$ NMR measurement, neat samples were flame-sealed in thin-walled 3 mm o.d. capillaries and placed into 5 mm NMR tubes, using $CDCl_3$ as an external

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[43] *SHELTX-Plus, a Complex Software Package for Solving, Refining and Displaying Crystal Structures*, version SGI IRIS Indigo; Siemens: Munich, Germany, 1991.

reference. The spectra were recorded with the spectrometer operating at 282.41 MHz.

**(D) UV−Visible Spectroscopy.** UV−visible spectra in the 200−600 nm range of gaseous sample was recorded using a glass cell equipped with quartz windows.

**(E) Melting Point Determination.** The melting point was determined for a small, tensimetrically pure sample contained in a 6 mm o.d. glass tube, itself immersed in cold ethanol bath; the temperature was measured with a thermometer attached to the tube.

**(F) Theoretical Calculations.** All quantum chemical calculations were performed with a commercial program package.[44] For the normal coordinate analysis, transformation of the ab initio Cartesian harmonic force constants to the molecule-fixed internal coordinates system were performed, as implemented in the ASYM40 program.[45] The internal and symmetry coordinates used to perform the normal coordinate analysis are defined in Figure S1 and Table S6, respectively, provided as Supporting Information.

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**Supporting Information Available:** Calculated relative energies (corrected by zero-point energy) and vibrational data are given in Tables S1 and S2, respectively. Crystallographic details data and listing of atomic coordinates and equivalent isotropic displacement coefficients and anisotropic displacement parameters for $CH_3OC(O)SNCO$ are given in Tables S3−S5. Definitions for symmetry and internal coordinates are listed in Table S6 and Figure S1, respectively. Electronic energies (E), zero point energies (ZPE), and number of imaginary frequencies obtained from HF and DFT calculations are given in Table S7. Cartesian coordinates of the optimized structures by the HF and DFT methods (Tables S8−S29). $^1H$ and $^{13}C$ NMR spectra and X-ray crystallographic data in CIF format are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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