**Supporting Information**

# Vibrational and Valence Photoelectron Spectroscopies, Matrix Photochemistry and Conformational Studies of ClC(O)SSCl

*Yeny A. Tobón,*[a] *Melina V. Cozzarín,*[a] *Wei-Gang Wang,*[b] *Mao-Fa Ge,*[b] *Carlos O. Della Védova,*[a,c] *and Rosana M. Romano*[a*]

**Table S1**. Cartesian coordinates of the *syn-gauche* optimized structure of ClC(O)SSCl at the B3LYP/6-31+G* level of approximation

| Atom | X | Y | Z |
|---|---|---|---|
| Cl | -2.936345 | 0.081831 | -0.379266 |
| C | -1.297870 | 0.383309 | 0.278463 |
| S | -0.227284 | -1.005614 | -0.208090 |
| S | 1.548788 | -0.574238 | 0.709970 |
| Cl | 2.626641 | 0.638294 | -0.620950 |
| O | -1.011485 | 1.341955 | 0.912852 |

**Table S2**. Cartesian coordinates of the *anti-gauche* optimized structure of ClC(O)SSCl at the B3LYP/6-31+G* level of approximation

| Atom | X | Y | Z |
|---|---|---|---|
| Cl | -1.496694 | 1.465571 | 0.270830 |
| C | -1.681208 | -0.229760 | -0.216525 |
| S | -0.255147 | -1.359407 | -0.022596 |
| S | 1.277447 | -0.353271 | 0.865619 |
| Cl | 2.393565 | 0.544395 | -0.674024 |
| O | -2.689546 | -0.673501 | -0.666864 |

**Table S3**. Cartesian coordinates of the *syn-gauche* optimized structure of ClC(O)SSCl at the MP2/6-31+G* level of approximation

| Atom | X | Y | Z |
|---|---|---|---|
| Cl | -2.873338 | 0.130854 | -0.328682 |
| C | -1.233666 | 0.346631 | 0.276589 |
| S | -0.223163 | -1.038260 | -0.257411 |
| S | 1.536886 | -0.628145 | 0.663186 |
| Cl | 2.486952 | 0.705532 | -0.584978 |
| O | -0.881124 | 1.295517 | 0.922532 |

**Table S4**. Cartesian coordinates of the *anti-gauche* optimized structure of ClC(O)SSCl at the MP2/6-31+G* level of approximation

| Atom | X | Y | Z |
|---|---|---|---|
| Cl | -1.381868 | 1.459614 | 0.294838 |
| C | -1.637210 | -0.201354 | -0.195396 |
| S | -0.266523 | -1.364030 | -0.052856 |
| S | 1.265388 | -0.401389 | 0.845650 |
| Cl | 2.282097 | 0.557712 | -0.671443 |
| O | -2.682809 | -0.604964 | -0.638757 |

**Table S5.** Calculated vibrational wavenumbers ($cm^{-1}$), relative IR and Raman intensities and tentative assignment for the *syn-gauche* conformer of ClC(O)SSCl

| B3LYP/6-31+G* | | | MP2/6-31+G* | | Assignment |
|---|---|---|---|---|---|
| Wavenumbers [$cm^{-1}$] | $I_{IR}$ | $I_{Raman}$ | Wavenumbers [$cm^{-1}$] | $I_{IR}$ | |
| 1863.6 | (58) | (61) | 1795.3 | (43) | $\nu$ (C=O) |
| 796.1 | (100) | (8) | 857.7 | (100) | $\nu_{as}$ (Cl-C-S) |
| 567.0 | (1) | (12) | 574.1 | (1) | $\delta_{oop}$ (C=O) |
| 554.1 | (3) | (61) | 593.6 | (2) | $\nu_{s}$ (Cl-C-S) |
| 495.4 | (<1) | (11) | 536.8 | (1) | $\nu$ (S-S) |
| 450.1 | (13) | (100) | 497.8 | (9) | $\nu$ (S-Cl) |
| 414.3 | (4) | (18) | 441.5 | (2) | $\delta$ (Cl-C=O) |
| 269.5 | (2) | (13) | 289.5 | (2) | $\delta$ (Cl-C-S) |
| 190.4 | (<1) | (29) | 205.1 | (<1) | $\delta$ (S-S-Cl) |
| 161.5 | (<1) | (5) | 177.8 | (<1) | $\delta$ (C-S-S) |
| 69.7 | (<1) | (11) | 63.12 | (<1) | $\tau$ (C-S-S-Cl) |
| 56.2 | (<1) | (8) | 55.9 | (<1) | $\tau$ (Cl-C-S-S) |

**Table S6.** Calculated vibrational wavenumbers ($cm^{-1}$), relative IR and Raman intensities and tentative assignment for the *anti-gauche* conformer of ClC(O)SSCl

| B3LYP/6-31+G* | | | MP2/6-31+G* | | Assignment |
|---|---|---|---|---|---|
| Wavenumbers [$cm^{-1}$] | $I_{IR}$ | $I_{Raman}$ | Wavenumbers [$cm^{-1}$] | $I_{IR}$ | |
| 1832.0 | (98) | (100) | 1765.9 | (82) | ν (C=O) |
| 839.5 | (100) | (2) | 891.5 | (100) | $\nu_{as}$ (Cl-C-S) |
| 563.2 | (1) | (<1) | 573.3 | (1) | $\delta_{oop}$ (C=O) |
| 496.5 | (3) | (54) | 525.9 | (3) | $\nu_{s}$ (Cl-C-S) |
| 513.5 | (2) | (17) | 554.0 | (3) | ν (S-S) |
| 442.4 | (18) | (92) | 490.6 | (13) | ν (S-Cl) |
| 385.4 | (1) | (16) | 405.1 | (2) | δ (Cl-C=O) |
| 326.2 | (3) | (23) | 344.8 | (2) | δ (Cl-C-S) |
| 200.3 | (1) | (28) | 210.7 | (<1) | δ (S-S-Cl) |
| 162.3 | (<1) | (8) | 178,0 | (<1) | δ (C-S-S) |
| 71.6 | (<1) | (11) | 72.9 | (<1) | τ (C-S-S-Cl) |
| 46.2 | (<1) | (5) | 43.2 | (<1) | τ (Cl-C-S-S) |

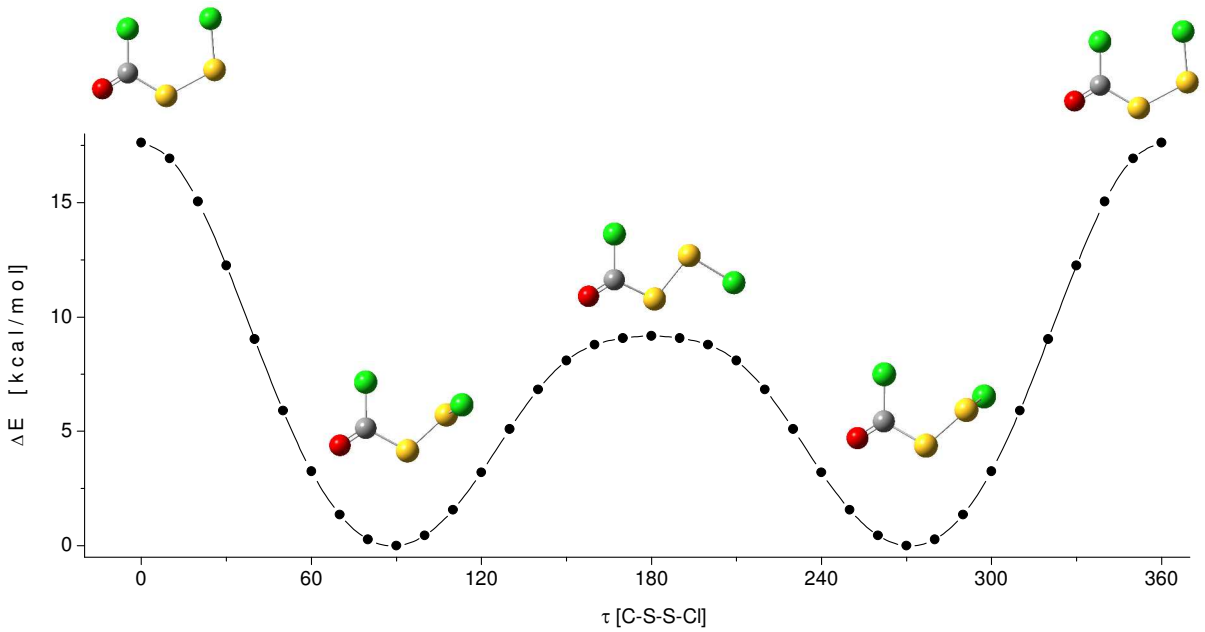


**Figure S1.** Potential energy curve for *anti*-ClC(O)SSCl around the S-S single bond from 0 to 360° in steps of 10° calculated at the B3LYP/6-31+G* level of approximation by a relaxed scan.

## Gas Chromatography – Mass Spectrometry

A 200 ppm solution of ClC(O)SSCl in $CCl_4$ was prepared and analyzed by GC-MS with the following parameters:

| | |
|---|---|
| Carrier gas: | He |
| Column: | 19091J-433 HP-5 |
| Length: | 30 m |
| I.D: | 0.25 mm |
| Film: | 0.25 μm |
| Injection volume: | 1 μl |
| Column oven temperature: | 60 °C |
| Injection temperature: | 200 °C |
| Injection mode: | Split |
| Flow control mode: | Pressure |
| Pressure: | 120.0 kPa |
| Total flow: | 43.8 ml/min |
| Column flow: | 1.94 ml/min |
| Linear velocity: | 50.9 cm/s |
| Purge flow: | 3.0 ml/min |
| Split ratio: | 20.0 |

Oven temperature program:

| Rate (°C/min) | Temperature (°C) | Hold time (min) |
|---|---|---|
| - | 60 | 3 |
| 10 | 150 | 1 |
| 50 | 200 | 1 |

Pressure program:

| Rate (kPa/min) | Pressure (kPa) | Hold time (min) |
|---|---|---|
| - | 120 | 2 |
| 7 | 210 | 1 |

| | |
|---|---|
| Ions source temperature: | 200.0 °C |
| Interface temperature: | 250.0 °C |
| Solvent cut time: | 3 min |
| Acquisition mass range: | 2 - 500 |
| Ionization energy: | 70 eV |

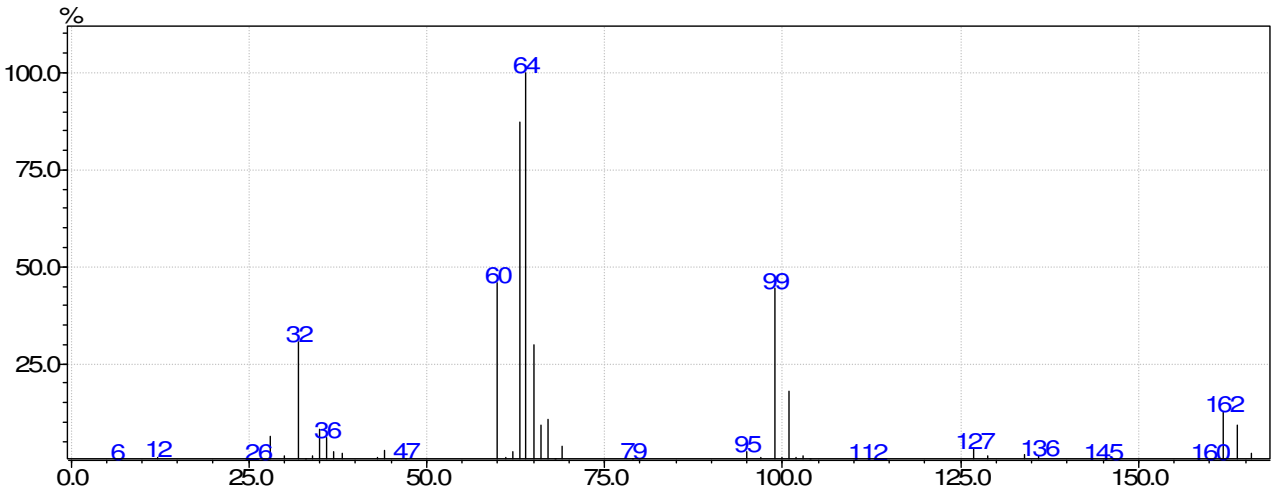


**Figure S2**. Mass spectrum of ClC(O)SSCl