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

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**Table S1.** Calculated relative energies (corrected by zero-point energy) in kcal $mol^{-1}$ for the different conformers to the $CH_3OC(O)SNCO$

| Method | | syn-syn-syn | syn-syn-anti | syn-anti-syn | syn-anti-anti | anti-syn-syn |
|---|---|---|---|---|---|---|
| **HF** | **6-31G*** | 0.00 | 2.15[a] | 1.86 | 3.01 | 8.70 |
| | **6-311++G**** | 0.00 | 1.64[a] | 1.61 | 2.57[a] | 8.27 |
| **B3LYP** | **6-31G*** | 0.00 | 1.75 | 1.80 | 2.68 | 5.91 |
| | **6-311++G**** | 0.00 | 1.10 | 1.33 | 2.02 | 5.93 |

[a] One imaginary frequency has been calculated for this form.

**Table S2.** Observed and Calculated Vibrational data ($cm^{-1}$) for $CH_3OC(O)SNCO$

| Experimental | | | Calculated[c] | | Assignment/ Approximated description (P. E. D.)[d]/ Symmetry |
|---|---|---|---|---|---|
| Mode | IR[a] | Raman[b] | B3LYP/6-311++G** | | |
| | | | *syn-syn-syn* | *syn-syn-anti* | |
| | 3598 | | | | $\nu_3 + \nu_7$ |
| | 3044 | | | | $\nu_3 + \nu_{12}$ |
| $\nu_1$ | 3016 vw | 3046 | 3173 (1) | 3171 (1) | $\nu_{as}(CH_3)$ (98) /A' |
| $\nu_2$ | 2857 vw | 2842 | 3060 (2) | 3058 (2) | $\nu_s(CH_3)$ (98) /A' |
| | 2345 | | | | $2 \times \nu_9$ |
| $\nu_3$ | 2248 vs | 2243 | 2333 (100) | 2349 (100) | $\nu_{as}$(NCO) (99) /A' |
| | 2191 | | | | $\nu_8 + \nu_{11}$ |
| | 2158 | | | | $\nu_9 + \nu_{11}$ |
| $\nu_4$ | 1784<br>1750 | 1734 | 1788 (16) | 1826 (21) | ν(C=O) (99) /A' |
| $\nu_5$ | 1443 vw | 1450 | 1495 (1) | 1496 (1) | $\delta_{as}(CH_3)$ (86) + $\rho(CH_3)$ (11) /A' |
| $\nu_6$ | 1368 vw | | 1468 (1) | 1468 (1) | $\delta_s(CH_3)$ (95) /A' |
| $\nu_7$ | 1336 vw | 1350 | 1417 (< 0.1) | 1425 (< 0.1) | $\nu_s$(NCO) (88) + ν(S–N) (13) /A' |
| $\nu_8$ | 1195 sh | 1193 | 1212 (19) | 1210 (9) | $\nu_{as}$(COC) (22)+ $\rho_s(CH_3)$ (62) /A' |
| $\nu_9$ | 1171 vs | 1148 | 1181 (48) | 1169 (48) | $\nu_{as}$(COC) (54) + $\rho_s(CH_3)$ (17) + δ(OC=OS) (24) /A' |
| $\nu_{10}$ | | 940 | 959 (< 0.1) | 961 (< 0.1) | $\nu_s$(COC) (84) + $\nu_{as}$(COC) (22) /A' |
| $\nu_{11}$ | 822 w | 821 | 826 (2) | 825 (2) | ν(C–S) (19) + δ(OCO) (24) + δ(COC) (19) /A' |
| $\nu_{12}$ | 706 vw | 701 | 677 (4) | 673 (1) | ν(S–N) (65) + δ(OC=OS) (35) /A' |
| $\nu_{13}$ | 615 vw<br>604 w | 598 | 598 (2) | 616 (2) | ν(S–N) (26) + δ(NCO) (55) /A' |
| $\nu_{14}$ | 513 vw | 511 | 506 (1) | 499(< 0.1) | ν(CS) (46) + δ (O=CS) (21) + $\delta_s$ (CSN) (24) /A' |
| $\nu_{15}$ | | 383 | 367 (1) | 358 (1) | ν(C–S (26) + δ (OCS) (21) + δ (COC) (22) /A' |

| | | | | | |
|---|---|---|---|---|---|
| $\nu_{16}$ | | 321 | 311 (3) | 272 (< 0.1) | $\delta_{as}$(COC) (28) + $\delta_{as}$(CSN) (40) + δ (SNC) (13) + δ(OC=OS) (19) /A' |
| $\nu_{17}$ | | 212 | 213 (< 0.1) | 199 (1) | $\delta_{s}$(COC) (26) + $\delta_{s}$(SNC) (38) + δ (O=CS) (36) /A' |
| $\nu_{18}$ | | | 88 (< 0.1) | 80 (< 0.1) | $\delta_{s}$(SNC) (69) + δ(O=CS) (18) + $\delta_{as}$(CSN) (15) /A' |
| $\nu_{19}$ | 2967 w | 2962 | 3140 (1) | 3137 (1) | $\nu_{as}$ ($CH_3$ (100) /A" |
| $\nu_{20}$ | 1436 vw | 1410 | 1484 (1) | 1484 (1) | $\delta_{as}$ ($CH_3$ (93) + $\rho_s$ $CH_3$ (7) /A" |
| $\nu_{21}$ | | | 1167 (< 0.1) | 1168 (< 0.1) | $\rho_{as}$ ($CH_3$ (91) + $\delta_{as}$ $CH_3$ (8) /A" |
| $\nu_{22}$ | 681 vvw 668 vvw | | 661 (1) | 662 (1) | oop (C=O) (100) /A" |
| $\nu_{23}$ | 556 vw | 546 | 558 (2) | 557 (2) | oop (NCO) (100) /A" |
| $\nu_{24}$ | | | 145 (< 0.1) | 139(< 0.1) | $\rho_{as}$($OCH_3$) (17)+ τ(COC=O) (40) + τ(O=CSN) (43) /A" |
| $\nu_{25}$ | | | 109 (< 0.1) | 107 (< 0.1) | τ(COC=O) (20) + τ(O=CSN) (65) /A" |
| $\nu_{26}$ | | | 101(< 0.1) | 100 (< 0.1) | $\rho_{s}$($CH_3$) (60) + τ(O=CSN) (40) /A" |
| $\nu_{27}$ | | | 29 (< 0.1) | 24 (< 0.1) | τ(SNCO) (100) /A" |

[a] band intensity: vs = very strong, s = strong, m = medium, sh = shoulder, w = weak, vw = very weak, vvw = very very weak; [b] liquid at room temperature; [c] In parentheses relative band strength; [d] potential energy distribution expressed in percent.

**Table S3.** Crystal data for $CH_3OC(O)SNCO$

| | |
|---|---|
| Empirical formula | $C_3H_3NO_3S$ |
| Formula weight | 133.12 |
| Wavelength | 0.71073 Å |
| Temperature | 203(2) K |
| Crystal size | 0.3 mm |
| Crystal color | colorless |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | $a$ = 8.2923(6) Å |
| | $b$ = 9.8389(7) Å |
| | $c$ = 11.8651(8) Å |
| | $\alpha$ = 67.290(2) º |
| | $\beta$ = 71.5570 (10) º |
| | $\gamma$ = 83.4850 (10) º |
| Volume | 847.08(10) $Å^3$ |
| Z | 6 |
| Density (calculated) | 1.566 g $cm^{-3}$ |
| Absorption Coefficient | 0.486 $mm^{-1}$ |
| F(000) | 408 |

**Table S4.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for $CH_3OC(O)SNCO$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 6691 | –3391 | 7745 | 82 |
| H(1B) | 6492 | –3684 | 9193 | 82 |
| H(1C) | 7905 | –2571 | 8081 | 82 |
| S(1) | 4146(1) | 657(1) | 7348(1) | 42(1) |
| O(1) | 5549(2) | –1745(2) | 8291(2) | 47(1) |
| N(1) | 4561(2) | 1847(2) | 5845(2) | 43(1) |
| C(1) | 2762(3) | –2948(2) | 8330(2) | 54(1) |
| O(2) | 6750(1) | –591(1) | 6168(1) | 45(1) |
| C(2) | 5723(2) | –693(2) | 7169(2) | 35(1) |
| C(3) | 5627(2) | 1891(2) | 4874(2) | 42(1) |
| O(3) | 6562(2) | 2098(2) | 3870(2) | 62(1) |

**Table S5.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $CH_3OC(O)SNCO$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [ h^2 a^{*2} U11 + ... + 2 h k a^* b^* U_{12} ]$

| | **U11** | **U22** | **U33** | **U23** | **U13** | **U12** |
|---|---|---|---|---|---|---|
| S(1) | 44(1) | 45(1) | 36(1) | -17(1) | -11(1) | 14(1) |
| O(1) | 58(1) | 42(1) | 33(1) | -9(1) | -14(1) | 17(1) |
| N(1) | 47(1) | 41(1) | 35(2) | -10(1) | -14(1) | 15(1) |
| C(1) | 66(1) | 43(1) | 52(2) | -14(1) | -25(1) | 22(1) |
| O(2) | 42(1) | 46(1) | 39(1) | -15(1) | -8(1) | 11(1) |
| C(2) | 37(1) | 35(1) | 35(2) | -14(1) | -14(1) | 5(1) |
| C(3) | 47(1) | 33(1) | 45(2) | -13(1) | -17(1) | 10(1) |
| O(3) | 69(1) | 50(1) | 42(1) | -8(1) | -1(1) | 14(1) |

**Table S6.** Symmetry coordinates for methoxycarbonylsulfenyl isocyanate, $CH_3OC(O)SNCO$

| Species | Description | Symmetry coordinate [a] (not normalized) |
|---|---|---|
| A' | $CH_3$ antisymmetric strechting | $S_1 = 2r_1 - r_2 - r_3$ |
| | $CH_3$ symmetric strechting | $S_2 = r_1 + r_2 + r_3$ |
| | NCO antisymmetric strechting | $S_3 = P - T$ |
| | C=O strechting | $S_4 = R$ |
| | NCO symmetric strechting | $S_5 = P + T$ |
| | COC antisymmetric strechting | $S_6 = D - S$ |
| | COC symmetric strechting | $S_7 = D + S$ |
| | C–S strechting | $S_8 = H$ |
| | S=N strechting | $S_9 = Q$ |
| | $CH_3$ antisymmetric deformation | $S_{10} = 2\alpha_1 - \alpha_2 - \alpha_3$ |
| | $CH_3$ symmetric deformation | $S_{11} = \alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3$ |
| | $CH_3$ rocking | $S_{12} = 2\beta_1 - \beta_2 - \beta_3$ |
| | NCO bending | $S_{13} = \mu$ |
| | OC(O)S bending | $S_{14} = \gamma + \varepsilon$ |
| | OCS deformation | $S_{15} = 2\delta - \varepsilon - \gamma$ |
| | SNC bending | $S_{16} = \sigma$ |
| | COC bending | $S_{17} = \rho$ |
| | CSN bending | $S_{18} = \varphi$ |
| | Redundancy | $S_{1R} = \delta + \varepsilon + \gamma$ |
| | Redundancy | $S_{2R} = \alpha_1 + \alpha_2 + \alpha_3 + \beta_1 + \beta_2 + \beta_3$ |
| A" | $CH_3$ antisymmetric strechting | $S_{19} = r_2 - r_3$ |
| | $CH_3$ antisymmetric deformation | $S_{20} = \alpha_2 - \alpha_3$ |
| | $CH_3$ rocking | $S_{21} = \beta_2 - \beta_3$ |
| | NCO out of plane (oop) | $S_{22} = \pi$ |
| | OC(O)S out of plane (oop) | $S_{23} = \omega$ |
| | $CH_3$ torsion | $S_{24} = \tau_1$ |
| | NCO torsion | $S_{25} = \tau_2$ |
| | COC(O) torsion | $S_{26} = \tau_3$ |
| | C(O)SN torsion | $S_{27} = \tau_4$ |

[a] see figure S1 for internal coordinates

**Table S7.** Electronic Energies (E), Zero Point Energies (ZPE), and Number of Imaginary Frequencies for Conformers of $CH_3OC(O)SNCO$ calculated at different Levels of Approximation.

| Conformer | Method | E, hartree | ZPE, hartree | Nº of imag. frequencies |
|---|---|---|---|---|
| (*syn-syn-syn*) | HF/6-31+G* | -791.886028 | 0.072795 | 0 |
| | HF/6-311++G** | -792.019582 | 0.071980 | 0 |
| | B3LYP/6-31+G* | -794.717941 | 0.066889 | 0 |
| | B3LYP/6-311++G** | -794.8693546 | 0.066222 | 0 |
| (*syn-syn-anti*) | HF/6-31+G* | -791.8823828 | 0.072568 | 1 |
| | HF/6-311++G** | -792.0167886 | 0.071802 | 1 |
| | B3LYP/6-31+G* | -794.7150245 | 0.066759 | 0 |
| | B3LYP/6-311++G** | -794.867522 | 0.066145 | 0 |
| (*syn-anti-syn*) | HF/6-31+G* | -791.882957 | 0.072689 | 0 |
| | HF/6-311++G** | -792.0169392 | 0.071904 | 0 |
| | B3LYP/6-31+G* | -794.7148715 | 0.066679 | 0 |
| | B3LYP/6-311++G** | -794.8670766 | 0.066070 | 0 |
| (*syn-anti-anti*) | HF/6-31+G* | -791.8810145 | 0.072574 | 0 |
| | HF/6-311++G** | -792.0153212 | 0.071808 | 1 |
| | B3LYP/6-31+G* | -794.7134358 | 0.066653 | 0 |
| | B3LYP/6-311++G** | -794.8659442 | 0.066030 | 0 |
| (*anti-syn-syn*) | HF/6-31+G* | -791.8719903 | 0.072614 | 0 |
| | HF/6-311++G** | -792.0061745 | 0.071755 | 0 |
| | B3LYP/6-31+G* | -794.7083986 | 0.066764 | 0 |
| | B3LYP/6-311++G** | -794.859713 | 0.066023 | 0 |

**Table S8.** Cartesian Coordinates of the Optimized Structure for (*syn-syn-syn*) at the HF/6-31+G* Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | -0.366069 | -1.163936 | 0.000020 |
| C | -0.788978 | -0.059825 | -0.000098 |
| O | -2.047975 | 0.299365 | -0.000006 |
| S | 0.221302 | 1.400951 | -0.000133 |
| N | 1.751938 | 0.735985 | 0.000382 |
| C | 2.240195 | -0.358625 | 0.000115 |
| O | 2.837658 | -1.337135 | -0.000183 |
| C | -3.019141 | -0.746864 | 0.000072 |
| H | -3.974699 | -0.249945 | 0.000174 |
| H | -2.905454 | -1.355837 | 0.883823 |
| H | -2.905626 | -1.355801 | -0.883727 |

**Table S9.** Cartesian Coordinates of the Optimized Structure for (*syn-syn-anti*) at the HF/6-31+G* Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | -1.024415 | 1.383122 | -0.000394 |
| C | -1.071019 | 0.208507 | -0.000145 |
| O | -2.151306 | -0.540874 | 0.000327 |
| S | 0.318611 | -0.906604 | -0.000323 |
| N | 1.544391 | 0.234905 | -0.001170 |
| C | 2.735205 | 0.194828 | 0.000120 |
| O | 3.884006 | 0.248943 | 0.001063 |
| C | -3.404020 | 0.139886 | 0.000594 |
| H | -4.152219 | -0.635156 | 0.000958 |
| H | -3.492064 | 0.753661 | -0.882964 |
| H | -3.491516 | 0.753963 | 0.883998 |

**Table S10.** Cartesian Coordinates of the Optimized Structure for (*syn-anti-syn*) at the HF/6-31+G* Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | 2.250385 | -0.687137 | -0.000341 |
| C | 1.116449 | -0.354631 | -0.000037 |
| O | 0.658851 | 0.871256 | 0.000224 |
| S | -0.151046 | -1.602302 | -0.000048 |
| N | -1.598062 | -0.759050 | 0.000544 |
| C | -1.987681 | 0.369100 | 0.000027 |
| O | -2.467916 | 1.412836 | -0.000448 |
| C | 1.626972 | 1.923570 | 0.000175 |
| H | 1.054499 | 2.835599 | 0.000426 |
| H | 2.241655 | 1.855483 | -0.883900 |
| H | 2.242025 | 1.855225 | 0.883973 |

**Table S11.** Cartesian Coordinates of the Optimized Structure for (*syn-anti-anti*) at the HF/6-31+G* Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | 2.432888 | 0.442514 | 0.000000 |
| C | 1.327764 | 0.019231 | 0.000000 |
| O | 0.966050 | -1.231026 | 0.000000 |
| S | 0.000000 | 1.200577 | 0.000000 |
| N | -1.351735 | 0.201768 | 0.000000 |
| C | -2.529551 | 0.384800 | 0.000000 |
| O | -3.676696 | 0.467314 | 0.000000 |
| C | 2.018765 | -2.194629 | 0.000000 |
| H | 1.526889 | -3.152808 | 0.000000 |
| H | 2.627726 | -2.077815 | 0.883395 |
| H | 2.627726 | -2.077815 | -0.883395 |

**Table S12.** Cartesian Coordinates of the Optimized Structure for (*anti-syn-syn*) at the HF/6-31+G* Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | 0.135403 | 1.474638 | -0.001202 |
| C | -0.673135 | 0.617027 | -0.000404 |
| O | -1.964556 | 0.856993 | 0.000290 |
| S | -0.194519 | -1.111683 | 0.000206 |
| N | 1.463361 | -0.983648 | -0.001640 |
| C | 2.269732 | -0.092475 | 0.000152 |
| O | 3.149893 | 0.638888 | 0.001432 |
| C | -2.943595 | -0.169774 | 0.000589 |
| H | -3.892268 | 0.340363 | 0.000315 |
| H | -2.861497 | -0.780010 | 0.890118 |
| H | -2.861401 | -0.780712 | -0.888445 |

**Table S13.** Cartesian Coordinates of the Optimized Structure for (*syn-syn-syn*) at the HF/6-311++G** Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | -0.372833 | -1.166320 | 0.000409 |
| C | -0.794125 | -0.06703 | 0.000108 |
| O | -2.048098 | 0.296814 | -0.000154 |
| S | 0.221816 | 1.392035 | -0.000095 |
| N | 1.748605 | 0.727629 | 0.000372 |
| C | 2.255064 | -0.353406 | -0.000009 |
| O | 2.857692 | -1.319721 | -0.000345 |
| C | -3.034439 | -0.735440 | -0.000108 |
| H | -3.983072 | -0.223713 | -0.000363 |
| H | -2.929792 | -1.346395 | 0.885012 |
| H | -2.929506 | -1.346743 | -0.884955 |

**Table S14.** Cartesian Coordinates of the Optimized Structure for (*syn-syn-anti*) at the HF/6-311++G** Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | -1.018024 | 1.382022 | -0.000660 |
| C | -1.069880 | 0.212693 | -0.000244 |
| O | -2.147418 | -0.534193 | 0.000545 |
| S | 0.320463 | -0.903918 | -0.000544 |
| N | 1.546014 | 0.232293 | -0.001948 |
| C | 2.732714 | 0.195276 | 0.000157 |
| O | 3.874180 | 0.245659 | 0.001807 |
| C | -3.407479 | 0.133110 | 0.000997 |
| H | -4.147301 | -0.650997 | 0.001641 |
| H | -3.502585 | 0.746340 | -0.883839 |
| H | -3.501651 | 0.746913 | 0.885536 |

**Table S15.** Cartesian Coordinates of the Optimized Structure for (*syn-anti-syn*) at the HF/6-311++G** Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | 2.248006 | -0.695070 | -0.000467 |
| C | 1.120763 | -0.356265 | -0.000042 |
| O | 0.667309 | 0.866705 | 0.000298 |
| S | -0.154330 | -1.598954 | 0.000017 |
| N | -1.595388 | -0.751347 | 0.000493 |
| C | -1.990665 | 0.370260 | -0.000020 |
| O | -2.469016 | 1.406629 | -0.000473 |
| C | 1.626101 | 1.927778 | 0.000204 |
| H | 1.044884 | 2.835331 | 0.000511 |
| H | 2.242020 | 1.865453 | -0.885092 |
| H | 2.242510 | 1.865167 | 0.885139 |

**Table S16.** Cartesian Coordinates of the Optimized Structure for (*syn-anti-anti*) at the HF/6-311++G** Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | -2.172700 | -1.174185 | 0.001192 |
| C | -1.257649 | -0.430703 | 0.000296 |
| O | -1.297484 | 0.865495 | -0.000306 |
| S | 0.372556 | -1.143214 | -0.000392 |
| N | 1.346710 | 0.222600 | -0.002369 |
| C | 2.518198 | 0.418176 | -0.000082 |
| O | 3.627393 | 0.692772 | 0.001669 |
| C | -2.588931 | 1.473268 | 0.000097 |
| H | -2.402837 | 2.534963 | -0.000588 |
| H | -3.135709 | 1.181059 | 0.885169 |
| H | -3.136716 | 1.180097 | -0.884033 |

**Table S17.** Cartesian Coordinates of the Optimized Structure for (*anti-syn-syn*) at the HF/6-311++G** Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | 0.120385 | 1.480119 | -0.001046 |
| C | -0.681816 | 0.624302 | -0.000344 |
| O | -1.972566 | 0.851303 | 0.000103 |
| S | -0.189386 | -1.105063 | 0.000162 |
| N | 1.463862 | -0.969824 | -0.001535 |
| C | 2.280239 | -0.094202 | 0.000130 |
| O | 3.157980 | 0.627931 | 0.001348 |
| C | -2.941801 | -0.185284 | 0.000641 |
| H | -3.896107 | 0.315412 | 0.000965 |
| H | -2.853078 | -0.794548 | 0.891477 |
| H | -2.853791 | -0.794801 | -0.890088 |

**Table S18.** Cartesian Coordinates of the Optimized Structure for (*syn-syn-syn*) at the B3LYP/6-31+G* Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | -1.155069 | 0.439249 | 0.000000 |
| C | 0.000000 | 0.786434 | 0.000000 |
| O | 0.471650 | 2.036357 | 0.000000 |
| S | 1.409659 | -0.337016 | 0.000000 |
| N | 0.627306 | -1.832418 | 0.000000 |
| C | -0.544492 | -2.182284 | 0.000000 |
| O | -1.592097 | -2.711228 | 0.000000 |
| C | -0.531919 | 3.078165 | 0.000000 |
| H | 0.028390 | 4.012153 | 0.000000 |
| H | -1.155740 | 2.999055 | 0.893146 |
| H | -1.155740 | 2.999055 | -0.893146 |

**Table S19.** Cartesian Coordinates of the Optimized Structure for (*syn-syn-anti*) at the B3LYP/6-31+G* Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | -0.504922 | -1.678331 | 0.000000 |
| C | -0.948597 | -0.564339 | 0.000000 |
| O | -2.237921 | -0.195773 | 0.000000 |
| S | 0.000000 | 0.975944 | 0.000000 |
| N | 1.543757 | 0.266030 | 0.000000 |
| C | 2.658864 | 0.750862 | 0.000000 |
| O | 3.786022 | 1.087820 | 0.000000 |
| C | -3.188518 | -1.283543 | 0.000000 |
| H | -4.167896 | -0.806515 | 0.000000 |
| H | -3.057163 | -1.899199 | 0.892840 |
| H | -3.057163 | -1.899199 | -0.892840 |

**Table S20.** Cartesian Coordinates of the Optimized Structure for (*syn-anti-syn*) at the B3LYP/6-31+G* Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | -2.258117 | 0.795981 | 0.000000 |
| C | -1.123847 | 0.385754 | 0.000000 |
| O | 0.000000 | 1.106543 | 0.000000 |
| S | -0.830735 | -1.389250 | 0.000000 |
| N | 0.852218 | -1.612941 | 0.000000 |
| C | 1.831962 | -0.890249 | 0.000000 |
| O | 2.861207 | -0.322583 | 0.000000 |
| C | -0.184011 | 2.542334 | 0.000000 |
| H | 0.823213 | 2.956223 | 0.000000 |
| H | -0.733163 | 2.847904 | 0.893104 |
| H | -0.733163 | 2.847904 | -0.893104 |

**Table S21** Cartesian Coordinates of the Optimized Structure for (*syn-anti-anti*) at the B3LYP/6-31+G* Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | 2.477701 | 0.442102 | 0.000000 |
| C | 1.350200 | 0.010024 | 0.000000 |
| O | 0.967312 | -1.262787 | 0.000000 |
| S | 0.000000 | 1.194321 | 0.000000 |
| N | -1.372751 | 0.180805 | 0.000000 |
| C | -2.563424 | 0.429263 | 0.000000 |
| O | -3.735542 | 0.531642 | 0.000000 |
| C | 2.051656 | -2.220040 | 0.000000 |
| H | 1.566816 | -3.195436 | 0.000000 |
| H | 2.668040 | -2.091232 | 0.892525 |
| H | 2.668040 | -2.091232 | -0.892525 |

**Table S22.** Cartesian Coordinates of the Optimized Structure for (*anti-syn-syn*) at the B3LYP/6-31+G* Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | 1.202517 | 0.904076 | 0.000000 |
| C | 0.000000 | 0.916740 | 0.000000 |
| O | -0.711707 | 2.050226 | 0.000000 |
| S | -0.971176 | -0.630310 | 0.000000 |
| N | 0.266568 | -1.770143 | 0.000000 |
| C | 1.489594 | -1.687362 | 0.000000 |
| O | 2.652188 | -1.837028 | 0.000000 |
| C | -2.148712 | 2.012267 | 0.000000 |
| H | -2.462519 | 3.055870 | 0.000000 |
| H | -2.526962 | 1.516015 | 0.899863 |
| H | -2.526962 | 1.516015 | -0.899863 |

**Table S23.** Cartesian Coordinates of the Optimized Structure for (*syn-syn-syn*) at the B3LYP/6-311++G** Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | -1.153955 | 0.469284 | 0.000000 |
| C | 0.000000 | 0.797518 | 0.000000 |
| O | 0.492778 | 2.036391 | 0.000000 |
| S | 1.392006 | -0.348184 | 0.000000 |
| N | 0.590986 | -1.828163 | 0.000000 |
| C | -0.560405 | -2.213048 | 0.000000 |
| O | -1.596667 | -2.746433 | 0.000000 |
| C | -0.480853 | 3.110796 | 0.000000 |
| H | 0.107861 | 4.024066 | 0.000000 |
| H | -1.103285 | 3.049240 | 0.892530 |
| H | -1.10328 | 3.049240 | -0.892530 |

**Table S24.** Cartesian Coordinates of the Optimized Structure for (*syn-syn-anti*) at the B3LYP/6-311++G** Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | -0.502293 | -1.670589 | 0.000000 |
| C | -0.946041 | -0.563063 | 0.000000 |
| O | -2.233091 | -0.196324 | 0.000000 |
| S | 0.000000 | 0.977735 | 0.000000 |
| N | 1.543535 | 0.284056 | 0.000000 |
| C | 2.663905 | 0.735064 | 0.000000 |
| O | 3.786909 | 1.058988 | 0.000000 |
| C | -3.200289 | -1.273739 | 0.000000 |
| H | -4.170071 | -0.783336 | 0.000000 |
| H | -3.076166 | -1.887496 | 0.892233 |
| H | -3.076166 | -1.887496 | -0.892233 |

**Table S25.** Cartesian Coordinates of the Optimized Structure for (*syn-anti-syn*) at the B3LYP/6-311++G** Level of Approximation

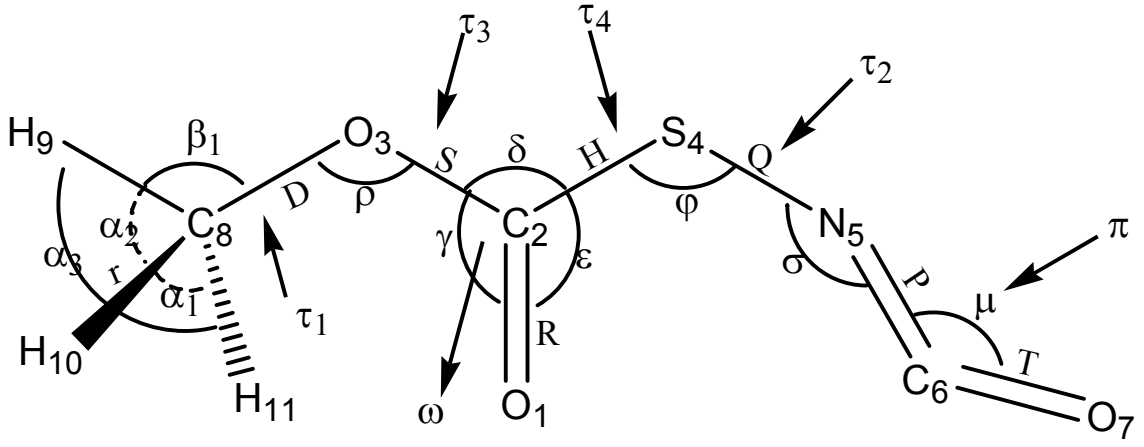
| Atom | X | Y | Z |
|---|---|---|---|
| O | -2.253228 | 0.816038 | 0.000000 |
| C | -1.126530 | 0.400439 | 0.000000 |
| O | 0.000000 | 1.109418 | 0.000000 |
| S | -0.845588 | -1.376709 | 0.000000 |
| N | 0.832249 | -1.600572 | 0.000000 |
| C | 1.832564 | -0.921079 | 0.000000 |
| O | 2.867323 | -0.380365 | 0.000000 |
| C | -0.153260 | 2.552911 | 0.000000 |
| H | 0.860868 | 2.942653 | 0.000000 |
| H | -0.693302 | 2.867181 | 0.892639 |
| H | -0.693302 | 2.867181 | -0.892639 |

**Table S26.** Cartesian Coordinates of the Optimized Structure for (*syn-anti-anti*) at the B3LYP/6-311++G** Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | 2.472162 | 0.452094 | 0.000000 |
| C | 1.349957 | 0.019841 | 0.000000 |
| O | 0.969040 | -1.248405 | 0.000000 |
| S | 0.000000 | 1.204069 | 0.000000 |
| N | -1.369414 | 0.195612 | 0.000000 |
| C | -2.559244 | 0.405436 | 0.000000 |
| O | -3.72514 | 0.489265 | 0.000000 |
| C | 2.042607 | -2.223013 | 0.000000 |
| H | 1.543863 | -3.188394 | 0.000000 |
| H | 2.656813 | -2.101602 | 0.892058 |
| H | 2.656813 | -2.101602 | -0.892058 |

**Table S27.** Cartesian Coordinates of the Optimized Structure for (a*nti-syn-syn*) at the B3LYP/6-311++G** Level of Approximation

| Atom | X | Y | Z |
|---|---|---|---|
| O | 1.195320 | 0.931565 | 0.000000 |
| C | 0.000000 | 0.934631 | 0.000000 |
| O | -0.727037 | 2.056029 | 0.000000 |
| S | -0.958907 | -0.622939 | 0.000000 |
| N | 0.281582 | -1.751942 | 0.000000 |
| C | 1.497985 | -1.718108 | 0.000000 |
| O | 2.650451 | -1.880539 | 0.000000 |
| C | -2.167268 | 2.003493 | 0.000000 |
| H | -2.489159 | 3.041750 | 0.000000 |
| H | -2.536782 | 1.506166 | 0.899651 |
| H | -2.536782 | 1.506166 | -0.899651 |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τ4
τ2
H9
β1
O3
S
δ
H
S4
Q
ρ
D
φ
α2
C8
γ
C2
N5
π
α3
r
ε
σ
P
μ
α1
τ1
R
H10
H11
ω
O1
C6
T
O7

**Figure S1**