# Disulfide Chromophores Arise from Stereoelectronic Effects

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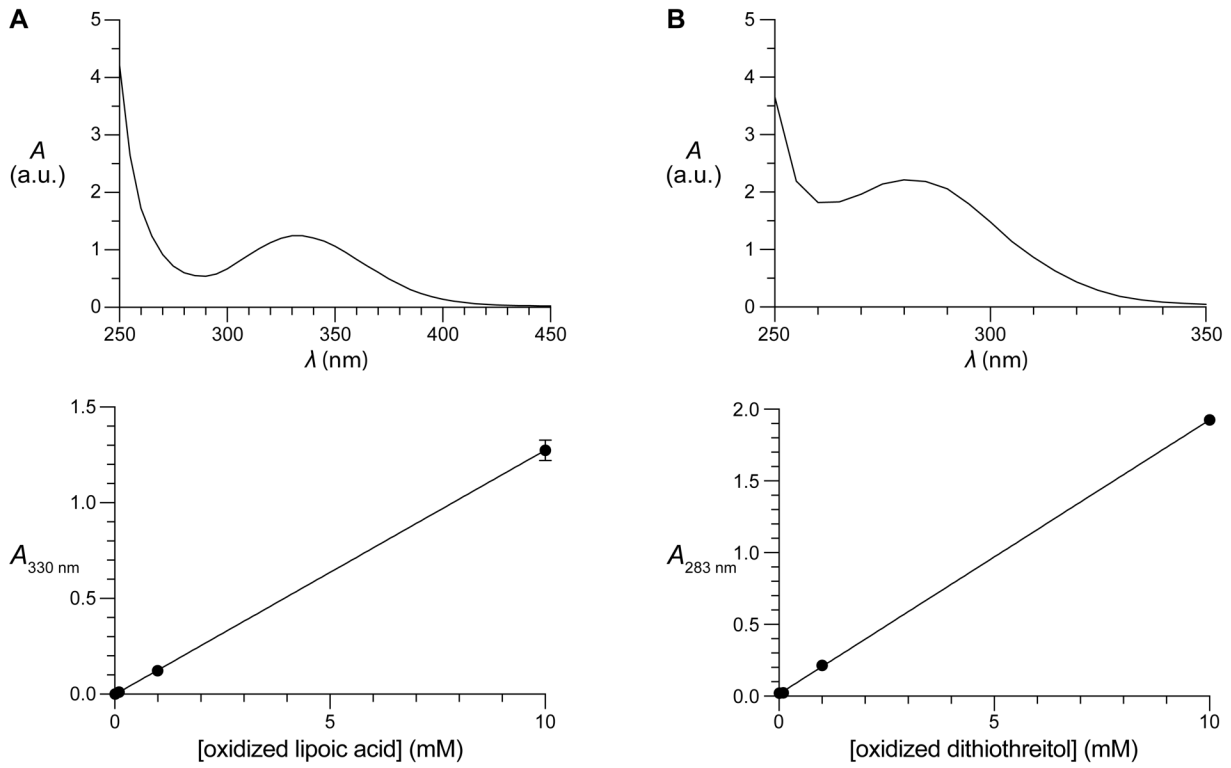


**Figure S1.** UV–vis spectroscopy of oxidized lipoic acid and oxidized dithiothreitol. (A) Spectrum of 10 mM oxidized lipoic acid ($\lambda_{max}$ = 330 nm) and concentration-dependence of absorbance at 330 nm ($\varepsilon$ = 128 $M^{-1}cm^{-1}$). (B) Spectrum of 10 mM oxidized dithiothreitol ($\lambda_{max}$ = 283 nm) and concentration-dependence of absorbance at 283 nm ($\varepsilon$ = 191 $M^{-1}cm^{-1}$). Data were obtained in 20 mM BIS-TRIS buffer, pH 7.5.

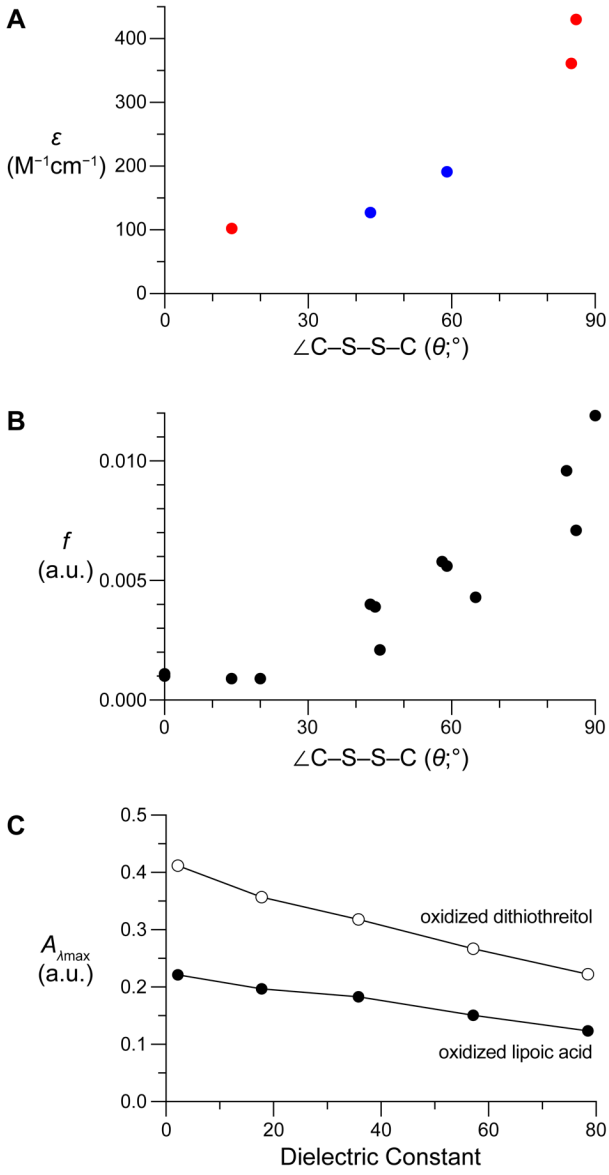


**Figure S2.** Dependence of the absorbance of disulfide bonds on their conformation and environment. (A) Graph of experimental extinction coefficients at $\lambda_{max}$ versus the computed C–S–S–C dihedral angle. Values were recorded in water (blue; Figure S1) or hexane (red). (B) Graph of computed oscillator strengths versus the computed C–S–S–C dihedral angle. (C) Graph of experimental absorbances of oxidized lipoic acid and oxidized dithiothreitol at $\lambda_{max}$ versus the dielectric constant of the solution. Values are listed in Table S1.

**Table S1. Physical and Photophysical Properties of Disulfides.**

| Compound | $\angle$C–S–S–C$^{comp}$ ($\theta$,°) | $\lambda_{max}^{exp}$ (nm) | $\lambda_{max}^{comp}$ (nm) | $\varepsilon^{exp}$ ($M^{-1}cm^{-1}$) | $f$ (a.u.) |
|---|---|---|---|---|---|
| dithiirane | 0 | | 458 | | 0.0010 |
| 1,2-dithietane | 20 | | 449 | | 0.0009 |
| 1,2-dithiolane | 44 | | 324 | | 0.0039 |
| 1,2-dithiane | 58 | | 304 | | 0.0058 |
| 1,2-dithiepane | 84 | | 270 | | 0.0096 |
| 1,2-dithiocane | 90 | | 266 | | 0.0119 |
| **1** | 64 | | 286 | | 0.0040 |
| **2** | 68 | | 281 | | 0.0010 |
| **3** | 88 | | 268 | | 0.0013 |
| **4** | 0 | 452[1] | 503 | | 0.0011 |
| **5** | 14 | 426[2] | 473 | 102[2] | 0.0009 |
| oxidized lipoic acid | 43 | 330 | 320 | 128 | 0.0040 |
| oxidized dithiothreitol | 59 | 283 | 302 | 191 | 0.0056 |
| dimethyl disulfide | 85 | 250[3] | 266 | 361[4] | 0.0087 |
| diethyl disulfide | 86 | 248[5] | 266 | 430[6] | 0.0071 |
| diethyl disulfide ($\theta$ = 45°) | 45 | | 325 | | 0.0021 |
| diethyl disulfide ($\theta$ = 65°) | 65 | | 291 | | 0.0043 |
| $CF_3SSCF_3$ | 83 | | 258 | | 0.0070 |

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(2) Nicolaou, K. C.; Hwang, C. K.; Duggan, M. E.; Carrol, P. J. Dithiatopazine. The First Stable 1,2-Dithietane. *J. Am. Chem. Soc.* **1987,** *109*, 3801–3802.

(3) Hearn, C. H.; Turcu, E.; Joens, J. A. The Near U.V. Absorption Spectra of Dimethyl Sulfide, Diethyl Sulfide, and Dimethyl Disulfide at *T*=300K. *Atmos. Environ.* **1990,** *24A*, 1939–1944.

(4) Rosenthal, N. A.; Oster, G. A. Ultraviolet Spectra of Alkyl Disulfides and Their Relation to Alkali Cleavage of Disulfide Bonds. *J. Am. Chem. Soc.* **1961,** *83*, 4445–4448.

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**Table S2.** Dithiirane (*n* = 1)

| | | | |
|---|---|---|---|
| C | 0.00000000 | 0.00000000 | 1.13826100 |
| H | 0.92046200 | 0.00000000 | 1.70660400 |
| H | -0.92046200 | 0.00000000 | 1.70660400 |
| S | 0.00000000 | 1.04575800 | -0.32008700 |
| S | 0.00000000 | -1.04575800 | -0.32008700 |

**Table S3.** 1,2-Dithietane (*n* = 2)

| | | | |
|---|---|---|---|
| C | 0.00000000 | 0.00000000 | 1.13826100 |
| H | 0.92046200 | 0.00000000 | 1.70660400 |
| H | -0.92046200 | 0.00000000 | 1.70660400 |
| S | 0.00000000 | 1.04575800 | -0.32008700 |
| S | 0.00000000 | -1.04575800 | -0.32008700 |

**Table S4.** 1,2-Dithiolane (*n* = 3)

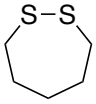
| | | | |
|---|---|---|---|
| C | 1.33780400 | -0.71300900 | -0.27852800 |
| C | 1.42657300 | 0.82704700 | -0.11497100 |
| C | 0.13863100 | 1.40153900 | 0.48072000 |
| H | 1.51854600 | -0.99871600 | -1.31355100 |
| H | 2.04780400 | -1.24092800 | 0.35827400 |
| H | 1.58643600 | 1.27366700 | -1.09705400 |
| H | 2.27845000 | 1.09805400 | 0.51283500 |
| H | 0.08750400 | 1.25271800 | 1.55992800 |
| H | 0.02246100 | 2.46185200 | 0.25136100 |
| S | -0.31941200 | -1.30301700 | 0.23913300 |
| S | -1.24054100 | 0.49426100 | -0.28882800 |

**Table S5.** 1,2-Dithiane (*n* = 4)

| | | | |
|---|---|---|---|
| C | -1.65511600 | 0.75161400 | 0.14610000 |
| C | -0.46020900 | 1.50607800 | -0.42836800 |
| C | -0.46025400 | -1.50606600 | 0.42837400 |
| C | -1.65513700 | -0.75157400 | -0.14610500 |
| H | -0.38424600 | 1.37726500 | -1.50916900 |
| H | -0.53787700 | 2.57299500 | -0.21101200 |
| H | -1.68641200 | 0.91396300 | 1.22728800 |
| H | -2.56835100 | 1.18662900 | -0.26994500 |
| H | -0.53794200 | -2.57298200 | 0.21103300 |

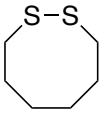
| | | | |
|---|---|---|---|
| H | -0.38428800 | -1.37723600 | 1.50917300 |
| H | -1.68643500 | -0.91392800 | -1.22729200 |
| H | -2.56838700 | -1.18656000 | 0.26994100 |
| S | 1.11680700 | -0.98442900 | -0.31949200 |
| S | 1.11683300 | 0.98440100 | 0.31949100 |

**Table S6.** 1,2-Dithiepane ($n$ = 5)




| | | | |
|---|---|---|---|
| C | -1.33283100 | 1.30096600 | -0.38217600 |
| C | -2.03033700 | -0.02936500 | -0.07159800 |
| C | -1.23128200 | -1.29279500 | -0.35779200 |
| C | -0.23309900 | 1.69828500 | 0.61818100 |
| C | 1.19929400 | 1.47030100 | 0.15246400 |
| H | -0.92541900 | 1.27744400 | -1.39775000 |
| H | -2.33820500 | -0.02930800 | 0.97816400 |
| H | -0.98657200 | -1.38010700 | -1.41667300 |
| H | -0.38587900 | 1.16676800 | 1.55942400 |
| H | 1.89892600 | 1.67119500 | 0.96301000 |
| H | -2.10198500 | 2.07578000 | -0.37747400 |
| H | -2.94865300 | -0.08949400 | -0.66495800 |
| H | -1.80605400 | -2.17621800 | -0.06957400 |
| H | -0.31585800 | 2.76305400 | 0.85352900 |
| H | 1.44322100 | 2.13399900 | -0.68088300 |
| S | 1.54896000 | -0.19434100 | -0.52935000 |
| S | 0.34079100 | -1.44925000 | 0.56052000 |

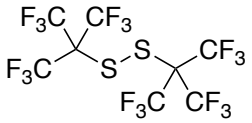
**Table S7.** 1,2-Dithiocane ($n$ = 6)




| | | | |
|---|---|---|---|
| C | -1.58989200 | -0.91662500 | 0.74757100 |
| C | -0.25084300 | 1.97003900 | -0.14888200 |
| C | -2.20667500 | 0.26131800 | -0.01943000 |
| C | -1.26632200 | 1.10405500 | -0.88220000 |
| H | -0.73312300 | 2.55520500 | 0.63996200 |
| H | -0.96911800 | -0.55059700 | 1.56713900 |
| H | -2.72125200 | 0.91558000 | 0.69327800 |
| H | -2.41644600 | -1.46021900 | 1.21309500 |
| H | 0.21282900 | 2.66544500 | -0.84918400 |
| H | -2.98310100 | -0.13910400 | -0.68062900 |
| H | -1.87840500 | 1.78843800 | -1.47934400 |
| H | -0.73796200 | 0.47297900 | -1.60242300 |
| C | 0.73673200 | -1.85535600 | 0.09392700 |
| H | 0.97625300 | -1.94362300 | 1.15565300 |
| H | 1.21389700 | -2.69288700 | -0.42278300 |
| C | -0.77517600 | -1.89810100 | -0.12100400 |

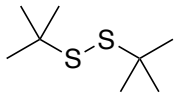
| | | | |
|---|---|---|---|
| H | -0.99803800 | -1.75079300 | -1.18259000 |
| H | -1.08540200 | -2.92164300 | 0.11208400 |
| S | 1.65282600 | -0.41428600 | -0.55906000 |
| S | 1.11173200 | 1.10611400 | 0.73505100 |

**Table S8.** Disulfide **1**



| | | | |
|---|---|---|---|
| C | 2.18500400 | 0.01637000 | -0.11438900 |
| C | -2.18004300 | -0.02904600 | -0.10326500 |
| S | -0.72037400 | -0.78540000 | -0.97485400 |
| S | 0.75837000 | 0.66115000 | -1.10339100 |
| C | 3.24616400 | 1.15929400 | -0.18718000 |
| C | -3.39993300 | -0.48306700 | -0.96196200 |
| C | 2.76844100 | -1.25636100 | -0.79316000 |
| C | 1.86930900 | -0.26823800 | 1.37565700 |
| C | -2.17234100 | 1.52007200 | -0.04137900 |
| C | -2.32238600 | -0.62252600 | 1.32473800 |
| F | -3.48887500 | 0.25542500 | -2.06220000 |
| F | -3.26418500 | -1.75762100 | -1.32784900 |
| F | -4.53627300 | -0.36976000 | -0.28438800 |
| F | -1.19745500 | -0.50004800 | 2.01012600 |
| F | -2.62227600 | -1.91751100 | 1.24912200 |
| F | -3.28717600 | -0.00978600 | 2.00768100 |
| F | -3.39048300 | 1.97362600 | 0.23894400 |
| F | -1.80405700 | 2.05249700 | -1.20341300 |
| F | -1.34101100 | 1.95212900 | 0.90120000 |
| F | 1.30701600 | -1.46797400 | 1.50576300 |
| F | 1.05209600 | 0.64631200 | 1.87465200 |
| F | 2.98571200 | -0.25759400 | 2.10262300 |
| F | 1.81416600 | -2.14392200 | -1.06735800 |
| F | 3.36059800 | -0.93191400 | -1.93916000 |
| F | 3.66119600 | -1.85243400 | -0.00955400 |
| F | 4.47153300 | 0.69303800 | 0.02923000 |
| F | 3.23467100 | 1.74122900 | -1.38543400 |
| F | 2.98111000 | 2.09086300 | 0.72196500 |

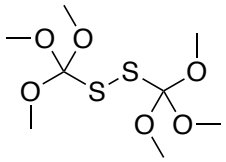
**Table S9.** Disulfide **2**



| | | | |
|---|---|---|---|
| C | -2.12237100 | 0.18281400 | -0.06051800 |
| C | 2.12236600 | 0.18283800 | 0.06049100 |
| S | 0.75430200 | -0.81570400 | -0.71040500 |
| S | -0.75427100 | -0.81557200 | 0.71047900 |
| C | -3.23476200 | 0.11896400 | 0.98811100 |
| H | -2.92241700 | 0.58274500 | 1.92663400 |

| | | | |
|---|---|---|---|
| H | -4.10966500 | 0.65822900 | 0.61429000 |
| H | -3.53049700 | -0.91314100 | 1.18948200 |
| C | 3.23478200 | 0.11894800 | -0.98810200 |
| H | 4.10966900 | 0.65822600 | -0.61427000 |
| H | 3.53055500 | -0.91316600 | -1.18939700 |
| H | 2.92245800 | 0.58267500 | -1.92665500 |
| C | -2.57170100 | -0.48058800 | -1.35961000 |
| H | -3.41966600 | 0.07098900 | -1.77791100 |
| H | -1.76659500 | -0.47569600 | -2.09747200 |
| H | -2.87870600 | -1.51343000 | -1.18516600 |
| C | -1.70486600 | 1.62481200 | -0.31503600 |
| H | -1.41451600 | 2.12376000 | 0.61146100 |
| H | -0.87024700 | 1.66762600 | -1.01745700 |
| H | -2.54532700 | 2.17230500 | -0.75327900 |
| C | 2.57172600 | -0.48043900 | 1.35964300 |
| H | 2.87887600 | -1.51325300 | 1.18528100 |
| H | 3.41961900 | 0.07125100 | 1.77794700 |
| H | 1.76661500 | -0.47560300 | 2.09750300 |
| C | 1.70476600 | 1.62483800 | 0.31487500 |
| H | 1.41444000 | 2.12369300 | -0.61168000 |
| H | 0.87011200 | 1.66766300 | 1.01725400 |
| H | 2.54516500 | 2.17242800 | 0.75311500 |

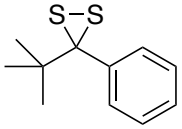
**Table S10.** Disulfide **3**



| | | | |
|---|---|---|---|
| C | -2.13327800 | -0.04536700 | 0.29982400 |
| C | 1.91300100 | -0.06907900 | -0.08284900 |
| S | 0.65355100 | 1.23332800 | -0.62859100 |
| S | -0.96680400 | 0.12733400 | -1.23997100 |
| O | -2.99595800 | -1.05529300 | -0.05260300 |
| O | -1.42527300 | -0.38089700 | 1.40980400 |
| O | -2.85278100 | 1.09334700 | 0.52857200 |
| O | 1.75520300 | -1.26314300 | -0.72600300 |
| O | 1.71031600 | -0.25546600 | 1.26584900 |
| O | 3.18486300 | 0.41544200 | -0.36918900 |
| C | -0.89394100 | -1.70302400 | 1.44401300 |
| H | -0.28711800 | -1.89720200 | 0.55653300 |
| H | -0.26731500 | -1.74020700 | 2.33163200 |
| H | -1.70411500 | -2.42904200 | 1.51596500 |
| C | -4.03397100 | -0.71820600 | -0.96898000 |
| H | -3.62844600 | -0.24354500 | -1.86588400 |
| H | -4.50568400 | -1.66136800 | -1.23550000 |
| H | -4.75696700 | -0.05129700 | -0.50063700 |
| C | -2.13732500 | 2.26131100 | 0.91000900 |
| H | -1.35324700 | 2.02045800 | 1.62835700 |
| H | -1.70363200 | 2.74110600 | 0.02979800 |

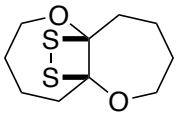
| | | | |
|---|---|---|---|
| H | -2.87282000 | 2.92379400 | 1.36194600 |
| C | 2.53443100 | -1.26261300 | 1.85267800 |
| H | 3.58768500 | -1.09064100 | 1.61835000 |
| H | 2.37713900 | -1.18315800 | 2.92672400 |
| H | 2.23989700 | -2.25293300 | 1.50182900 |
| C | 3.54728100 | 1.63410600 | 0.26576100 |
| H | 3.35651800 | 1.58677600 | 1.34002900 |
| H | 4.61196900 | 1.76327200 | 0.08276600 |
| H | 3.00376400 | 2.47813000 | -0.16744500 |
| C | 2.09987100 | -1.29789400 | -2.10741200 |
| H | 3.18060800 | -1.23071300 | -2.23241100 |
| H | 1.73072700 | -2.25116400 | -2.47882100 |
| H | 1.61571600 | -0.48019700 | -2.64596000 |

**Table S11.** Disulfide **4**




| | | | |
|---|---|---|---|
| C | 0.60938000 | -0.22770400 | -0.00013900 |
| S | 1.26763100 | -1.55513600 | -1.04960200 |
| S | 1.26774700 | -1.55528500 | 1.04904000 |
| C | -0.89827500 | -0.13238200 | -0.00004800 |
| C | -1.60465900 | -0.06947500 | -1.20060600 |
| C | -1.60466600 | -0.07024800 | 1.20054700 |
| C | -2.98811000 | 0.06677800 | -1.20225300 |
| H | -1.06707800 | -0.14027300 | -2.13990700 |
| C | -2.98812300 | 0.06599600 | 1.20225400 |
| H | -1.06708700 | -0.14175200 | 2.13979600 |
| C | -3.68373400 | 0.13770300 | 0.00002200 |
| H | -3.52246500 | 0.10792600 | -2.14385800 |
| H | -3.52249900 | 0.10652600 | 2.14387400 |
| H | -4.76252600 | 0.23755400 | 0.00005100 |
| C | 1.37016000 | 1.12610100 | 0.00018200 |
| C | 2.89254200 | 0.95190300 | -0.00226900 |
| H | 3.23390800 | 0.41725100 | -0.88917000 |
| H | 3.35556500 | 1.94130800 | 0.00033200 |
| H | 3.23619700 | 0.41149900 | 0.88026600 |
| C | 0.96785300 | 1.91821200 | -1.25202500 |
| H | -0.09744200 | 2.15478800 | -1.26125800 |
| H | 1.52353200 | 2.85862100 | -1.27878500 |
| H | 1.21141800 | 1.35853000 | -2.16035000 |
| C | 0.97131300 | 1.91535800 | 1.25529800 |
| H | 1.52609700 | 2.85629300 | 1.28209300 |
| H | -0.09416600 | 2.15094000 | 1.26845900 |
| H | 1.21842500 | 1.35407900 | 2.16166700 |

**Table S12.** Disulfide **5**




| | | | |
|---|---|---|---|
| C | 0.60938000 | -0.22770400 | -0.00013900 |
| S | 1.26763100 | -1.55513600 | -1.04960200 |
| S | 1.26774700 | -1.55528500 | 1.04904000 |
| C | -0.89827500 | -0.13238200 | -0.00004800 |
| C | -1.60465900 | -0.06947500 | -1.20060600 |
| C | -1.60466600 | -0.07024800 | 1.20054700 |
| C | -2.98811000 | 0.06677800 | -1.20225300 |
| H | -1.06707800 | -0.14027300 | -2.13990700 |
| C | -2.98812300 | 0.06599600 | 1.20225400 |
| H | -1.06708700 | -0.14175200 | 2.13979600 |
| C | -3.68373400 | 0.13770300 | 0.00002200 |
| H | -3.52246500 | 0.10792600 | -2.14385800 |
| H | -3.52249900 | 0.10652600 | 2.14387400 |
| H | -4.76252600 | 0.23755400 | 0.00005100 |
| C | 1.37016000 | 1.12610100 | 0.00018200 |
| C | 2.89254200 | 0.95190300 | -0.00226900 |
| H | 3.23390800 | 0.41725100 | -0.88917000 |
| H | 3.35556500 | 1.94130800 | 0.00033200 |
| H | 3.23619700 | 0.41149900 | 0.88026600 |
| C | 0.96785300 | 1.91821200 | -1.25202500 |
| H | -0.09744200 | 2.15478800 | -1.26125800 |
| H | 1.52353200 | 2.85862100 | -1.27878500 |
| H | 1.21141800 | 1.35853000 | -2.16035000 |
| C | 0.97131300 | 1.91535800 | 1.25529800 |
| H | 1.52609700 | 2.85629300 | 1.28209300 |
| H | -0.09416600 | 2.15094000 | 1.26845900 |
| H | 1.21842500 | 1.35407900 | 2.16166700 |

**Table S13.** Oxidized Lipoic Acid

| | | | |
|---|---|---|---|
| C | -2.78908473 | 6.56376113 | -6.93561926 |
| C | -2.11901871 | 7.09641643 | -5.64190632 |
| C | -2.75591125 | 6.48693542 | -4.39027370 |
| H | -3.16869619 | 7.38824550 | -7.53702546 |
| H | -2.10564798 | 5.97274683 | -7.54548117 |
| H | -2.24346877 | 8.17930614 | -5.60482935 |
| H | -1.04672552 | 6.88813208 | -5.65110092 |
| H | -2.39742577 | 5.47405654 | -4.20314778 |
| S | -4.16761302 | 5.43319197 | -6.50675987 |
| S | -4.54873360 | 6.41171024 | -4.70268704 |
| C | -2.51752289 | 7.35828602 | -3.14306918 |
| H | -1.46616506 | 7.44453259 | -2.96388148 |
| H | -2.93307234 | 8.33124198 | -3.30299215 |
| C | -3.19422337 | 6.70517660 | -1.92359202 |
| H | -4.21088485 | 7.03301218 | -1.86175948 |

| | | | |
|---|---|---|---|
| H | -3.16851252 | 5.64069301 | -2.02901323 |
| C | -2.44469554 | 7.11228977 | -0.64138030 |
| H | -2.39208056 | 8.17937610 | -0.58257184 |
| H | -1.45464875 | 6.70702835 | -0.66307204 |
| C | -3.19582136 | 6.56686970 | 0.58741055 |
| H | -4.18291275 | 6.97899347 | 0.61395447 |
| H | -3.25614438 | 5.50044415 | 0.52418326 |
| C | -2.43945322 | 6.96315514 | 1.86899749 |
| O | -1.16349295 | 7.60184839 | 1.77467710 |
| H | -0.80134619 | 7.72585644 | 2.65505868 |
| O | -2.94038355 | 6.72685600 | 2.99895416 |

**Table S14.** Oxidized Dithiothreitol

| | | | |
|---|---|---|---|
| C | -1.07073500 | 0.71401800 | 0.21060400 |
| C | 0.11083300 | 1.52467700 | -0.31731400 |
| C | 0.14790700 | -1.53058700 | 0.30743500 |
| C | -1.05546700 | -0.75516100 | -0.21260100 |
| H | 0.16455500 | 1.46214900 | -1.40580600 |
| H | -0.00003900 | 2.57426000 | -0.03038400 |
| H | -1.08480300 | 0.75143200 | 1.30731900 |
| H | 0.04801500 | -2.57555700 | 0.00709300 |
| H | 0.19728700 | -1.48096200 | 1.39654800 |
| H | -1.05800400 | -0.78642000 | -1.31121300 |
| S | 1.70950200 | -0.93872100 | -0.40528200 |
| S | 1.68493900 | 0.97595800 | 0.40809600 |
| O | -2.19735000 | -1.40526200 | 0.30350200 |
| H | -2.95823200 | -0.85743500 | 0.08100300 |
| O | -2.29253900 | 1.22188600 | -0.31737200 |
| H | -2.49596200 | 2.06605500 | 0.09264300 |

**Table S15.** $CF_3SSCF_3$

| | | | |
|---|---|---|---|
| C | -1.89556800 | 0.22704500 | -0.04673700 |
| C | 1.89554100 | 0.22708500 | 0.04663300 |
| S | 0.74088900 | -0.97131500 | -0.71372600 |
| S | -0.74081700 | -0.97096000 | 0.71408900 |
| F | 2.31288200 | -0.16794200 | 1.24500500 |
| F | 2.94905100 | 0.30551800 | -0.76323800 |
| F | 1.37367900 | 1.43769900 | 0.18344500 |
| F | -1.37359000 | 1.43750100 | -0.18431400 |
| F | -2.94884800 | 0.30611700 | 0.76331100 |
| F | -2.31328300 | -0.16871400 | -1.24478600 |

**Table S16.** Dimethyl Disulfide

| | | | |
|---|---|---|---|
| C | 1.78975000 | 0.81488600 | 0.39401600 |
| C | -1.78955100 | 0.81515300 | -0.39391400 |
| S | -0.91041000 | -0.50682300 | 0.49155900 |
| S | 0.91030200 | -0.50668600 | -0.49165900 |

| | | | |
|---|---|---|---|
| H | 1.28778200 | 1.77252200 | 0.26321300 |
| H | 1.86823600 | 0.57311500 | 1.45215000 |
| H | 2.78740600 | 0.87186000 | -0.04329300 |
| H | -2.78731400 | 0.87152600 | 0.04325700 |
| H | -1.28786200 | 1.77282300 | -0.26211900 |
| H | -1.86770400 | 0.57406600 | -1.45221100 |

**Table S17.** Diethyl Disulfide (unconstrained)

| | | | |
|---|---|---|---|
| C | 0.46452400 | 1.79964100 | 0.57555300 |
| H | 0.35524900 | 1.24779700 | 1.51001800 |
| H | 1.51760800 | 1.80805700 | 0.29509200 |
| C | -0.46452400 | -1.79964100 | 0.57555300 |
| H | -1.51760800 | -1.80805700 | 0.29509200 |
| H | -0.35524900 | -1.24779700 | 1.51001800 |
| S | 0.46452400 | -0.92280700 | -0.73375900 |
| S | -0.46452400 | 0.92280700 | -0.73375900 |
| C | -0.08766700 | 3.21295800 | 0.70779000 |
| H | -1.14402200 | 3.19930200 | 0.98254000 |
| H | 0.45794500 | 3.75582000 | 1.48183100 |
| H | 0.01536000 | 3.76304500 | -0.22939300 |
| C | 0.08766700 | -3.21295800 | 0.70779000 |
| H | -0.45794500 | -3.75582000 | 1.48183100 |
| H | -0.01536000 | -3.76304500 | -0.22939300 |
| H | 1.14402200 | -3.19930200 | 0.98254000 |

**Table S18.** Diethyl Disulfide ($\theta = 0°$)

| | | | |
|---|---|---|---|
| C | 1.55067100 | 0.80883400 | -0.02819700 |
| H | 1.18900700 | 1.28858100 | -0.93736100 |
| H | 1.12823900 | 1.31261500 | 0.84058500 |
| C | -1.55066300 | 0.80883400 | 0.02828100 |
| H | -1.12810800 | 1.31265100 | -0.84043400 |
| H | -1.18913900 | 1.28852600 | 0.93751500 |
| S | -1.06943200 | -0.94947600 | 0.01947600 |
| S | 1.06942300 | -0.94947700 | -0.01947500 |
| C | 3.07492100 | 0.85364400 | 0.02377500 |
| H | 3.51189300 | 0.34128600 | -0.83493400 |
| H | 3.41239000 | 1.89171000 | 0.00992100 |
| H | 3.44932700 | 0.38252900 | 0.93376900 |
| C | -3.07491100 | 0.85365100 | -0.02385300 |
| H | -3.41237100 | 1.89172000 | -0.00997300 |
| H | -3.44922500 | 0.38260000 | -0.93391800 |
| H | -3.51198800 | 0.34124700 | 0.83477500 |

**Table S19.** Diethyl Disulfide ($\theta = 10°$)

| | | | |
|---|---|---|---|
| C | -1.54626900 | 0.80232300 | -0.10136900 |
| H | -1.07713500 | 1.37566200 | 0.69702100 |
| H | -1.22919900 | 1.19890100 | -1.06657800 |

| | | | |
|---|---|---|---|
| C | 1.54626900 | 0.80232300 | 0.10136900 |
| H | 1.22919800 | 1.19890100 | 1.06657800 |
| H | 1.07713500 | 1.37566200 | -0.69702100 |
| S | 1.06720000 | -0.95094500 | -0.03596400 |
| S | -1.06720000 | -0.95094500 | 0.03596400 |
| C | -3.06555100 | 0.86232100 | 0.02423900 |
| H | -3.39391500 | 0.46924800 | 0.98758500 |
| H | -3.40014200 | 1.89825100 | -0.05655800 |
| H | -3.54800600 | 0.28518600 | -0.76625900 |
| C | 3.06555100 | 0.86232200 | -0.02423900 |
| H | 3.40014200 | 1.89825200 | 0.05655800 |
| H | 3.54800600 | 0.28518600 | 0.76625900 |
| H | 3.39391500 | 0.46924800 | -0.98758500 |

**Table S20.** Diethyl Disulfide ($\theta = 25°$)

| | | | |
|---|---|---|---|
| C | 1.54624900 | 0.78522500 | 0.16640300 |
| H | 1.05808000 | 1.44034600 | -0.55370800 |
| H | 1.24787300 | 1.07317000 | 1.17620500 |
| C | -1.54625100 | 0.78522200 | -0.16641400 |
| H | -1.24788900 | 1.07315600 | -1.17622400 |
| H | -1.05807000 | 1.44035000 | 0.55368300 |
| S | -1.04981100 | -0.94000900 | 0.14931000 |
| S | 1.04981100 | -0.94000800 | -0.14930900 |
| C | 3.06175000 | 0.85989900 | 0.01137500 |
| H | 3.36777700 | 0.55298000 | -0.99023500 |
| H | 3.39859400 | 1.88576200 | 0.17165000 |
| H | 3.56276900 | 0.21713800 | 0.73675300 |
| C | -3.06174900 | 0.85990100 | -0.01136500 |
| H | -3.39859400 | 1.88576200 | -0.17164600 |
| H | -3.56278000 | 0.21713200 | -0.73672800 |
| H | -3.36776200 | 0.55299300 | 0.99025300 |

**Table S21.** Diethyl Disulfide ($\theta = 45°$)

| | | | |
|---|---|---|---|
| C | 1.58087000 | 0.75048200 | 0.24331700 |
| H | 1.08793300 | 1.51281100 | -0.35926800 |
| H | 1.30996800 | 0.89236300 | 1.29159700 |
| C | -1.58089000 | 0.75044200 | -0.24340200 |
| H | -1.31010100 | 0.89221800 | -1.29172600 |
| H | -1.08787200 | 1.51281800 | 0.35905700 |
| S | -1.00414500 | -0.89399700 | 0.29655800 |
| S | 1.00415400 | -0.89399700 | -0.29655400 |
| C | 3.09170700 | 0.81437400 | 0.05078100 |
| H | 3.36176500 | 0.63198800 | -0.99119600 |
| H | 3.45972000 | 1.80432500 | 0.32674700 |
| H | 3.59745900 | 0.07346300 | 0.67152800 |
| C | -3.09170500 | 0.81438300 | -0.05070600 |
| H | -3.45972800 | 1.80431700 | -0.32671800 |
| H | -3.59753900 | 0.07342700 | -0.67133300 |

| | | | |
|---|---|---|---|
| H | -3.36165300 | 0.63209400 | 0.99131600 |

**Table S22.** Diethyl Disulfide ($\theta = 65°$)

| | | | |
|---|---|---|---|
| C | 1.67430700 | 0.68533100 | 0.36916800 |
| H | 1.14928900 | 1.55579500 | -0.02448600 |
| H | 1.52001900 | 0.63591700 | 1.44790000 |
| C | -1.67430200 | 0.68534300 | -0.36915300 |
| H | -1.51999300 | 0.63595100 | -1.44788300 |
| H | -1.14929500 | 1.55580000 | 0.02452900 |
| S | -0.96412100 | -0.82106100 | 0.38179300 |
| S | 0.96411900 | -0.82106100 | -0.38179500 |
| C | 3.15609400 | 0.75187700 | 0.01978000 |
| H | 3.30428500 | 0.77408400 | -1.06161100 |
| H | 3.59771300 | 1.65724100 | 0.44027600 |
| H | 3.69218300 | -0.10934700 | 0.42183600 |
| C | -3.15609600 | 0.75187300 | -0.01979100 |
| H | -3.59771100 | 1.65724400 | -0.44027700 |
| H | -3.69217300 | -0.10934400 | -0.42187500 |
| H | -3.30430700 | 0.77405700 | 1.06159800 |

**Table S23.** Diethyl Disulfide ($\theta = 80°$)

| | | | |
|---|---|---|---|
| C | 1.75145300 | 0.60452900 | 0.47259600 |
| H | 1.18974400 | 1.52139600 | 0.29007900 |
| H | 1.71764500 | 0.37894200 | 1.53847400 |
| C | -1.75145400 | 0.60452700 | -0.47259700 |
| H | -1.71764800 | 0.37893700 | -1.53847600 |
| H | -1.18974400 | 1.52139400 | -0.29008600 |
| S | -0.94208200 | -0.76779000 | 0.42539700 |
| S | 0.94208200 | -0.76779000 | -0.42539600 |
| C | 3.18538600 | 0.73816000 | -0.02387100 |
| H | 3.21339900 | 0.95550400 | -1.09325100 |
| H | 3.68776900 | 1.55239400 | 0.50165100 |
| H | 3.74868000 | -0.17972500 | 0.15402900 |
| C | -3.18538600 | 0.73816100 | 0.02387200 |
| H | -3.68776800 | 1.55239400 | -0.50165100 |
| H | -3.74868100 | -0.17972300 | -0.15402500 |
| H | -3.21339600 | 0.95550700 | 1.09325200 |

**Table S24.** Diethyl Disulfide ($\theta = 90°$)

| | | | |
|---|---|---|---|
| C | 1.82352400 | 0.55472600 | 0.50884600 |
| H | 1.28947600 | 1.50271700 | 0.43246900 |
| H | 1.82590000 | 0.23729700 | 1.55132200 |
| C | -1.82352400 | 0.55472600 | -0.50884600 |
| H | -1.82590000 | 0.23729700 | -1.55132200 |
| H | -1.28947600 | 1.50271700 | -0.43247000 |
| S | -0.92246200 | -0.70450400 | 0.46567600 |
| S | 0.92246200 | -0.70450400 | -0.46567600 |

| | | | |
|---|---|---|---|
| C | 3.23978700 | 0.67771800 | -0.03779000 |
| H | 3.23299000 | 0.98932900 | -1.08394600 |
| H | 3.79728800 | 1.42132900 | 0.53475500 |
| H | 3.77100600 | -0.27327300 | 0.03284900 |
| C | -3.23978700 | 0.67771800 | 0.03779000 |
| H | -3.79728800 | 1.42132900 | -0.53475500 |
| H | -3.77100600 | -0.27327300 | -0.03284900 |
| H | -3.23298900 | 0.98932900 | 1.08394600 |

## Anomeric Conformations of $XH_2C–S–S–CH_2X$

**Table S25.** X = Me

| | | | |
|---|---|---|---|
| C | 1.63128800 | 0.80927500 | -0.31116800 |
| C | -2.15524200 | -0.03157600 | 0.07345700 |
| S | -0.66914900 | -0.95204800 | 0.60787500 |
| S | 0.64641000 | -0.59354200 | -0.95145500 |
| H | -2.50098600 | -0.46548700 | -0.86540400 |
| H | 0.95431200 | 1.62859900 | -0.06784400 |
| H | 2.23620200 | 1.11399500 | -1.16923200 |
| H | -2.89116500 | -0.27098400 | 0.84537900 |
| C | 2.50524900 | 0.44044800 | 0.87643400 |
| H | 3.19985400 | -0.35879700 | 0.61378600 |
| H | 3.08049000 | 1.30863900 | 1.20747500 |
| H | 1.89043600 | 0.10185400 | 1.71227000 |
| C | -1.95864600 | 1.46957900 | -0.05485400 |
| H | -1.24104700 | 1.69373900 | -0.84641400 |
| H | -2.90338100 | 1.95195200 | -0.31702100 |
| H | -1.59677600 | 1.89958300 | 0.88108400 |

**Table S26.** X = OMe

| | | | |
|---|---|---|---|
| C | -1.41349800 | 0.35767000 | 0.70100500 |
| C | 2.03843100 | -0.36498600 | -0.34448400 |
| S | 0.55945000 | -1.27163300 | -0.84714200 |
| S | -0.52194800 | -1.20237100 | 0.91904400 |
| H | 2.44541600 | -0.81272900 | 0.56894200 |
| H | -0.69913000 | 1.11866500 | 0.37271700 |
| H | -1.80095800 | 0.61370700 | 1.69701800 |
| H | 2.75845000 | -0.48734500 | -1.16475800 |
| O | 1.73086500 | 0.98682800 | -0.13544000 |
| O | -2.45108400 | 0.19367000 | -0.22113000 |
| C | 2.83334200 | 1.70464500 | 0.37698200 |
| H | 3.68269200 | 1.67261800 | -0.31595600 |
| H | 2.51417200 | 2.73774000 | 0.50227000 |
| H | 3.14853000 | 1.30189400 | 1.34679700 |
| C | -3.01823000 | 1.42879100 | -0.59813400 |
| H | -3.81367800 | 1.21115900 | -1.30852100 |
| H | -3.44261400 | 1.95351100 | 0.26709600 |
| H | -2.27142100 | 2.07415200 | -1.07568800 |

**Table S27.** X = F

| | | | |
|---|---|---|---|
| C | -1.56625500 | 0.74592000 | 0.27004300 |
| C | 2.04396300 | 0.15683000 | 0.12206300 |
| S | 0.78569200 | -0.86629000 | -0.66086100 |
| S | -0.70152200 | -0.75513900 | 0.78218900 |
| H | 2.20246900 | -0.15366100 | 1.15369500 |
| H | -0.84895700 | 1.52319400 | 0.01315800 |
| H | -2.18879000 | 1.03934300 | 1.11756900 |
| H | 2.95338600 | 0.05249500 | -0.47182300 |
| F | 1.67523800 | 1.48616300 | 0.13464200 |
| F | -2.37869100 | 0.52105900 | -0.81314000 |

**Table S28.** X = Cl

| | | | |
|---|---|---|---|
| C | -1.36828000 | 0.61559800 | 0.70865100 |
| C | 2.15419200 | -0.47900700 | -0.18119900 |
| S | 0.58341900 | -1.14612900 | -0.76207500 |
| S | -0.57172800 | -0.98960000 | 0.94731900 |
| H | 2.44301500 | -0.94154300 | 0.75807900 |
| H | -0.63533200 | 1.37422600 | 0.45337700 |
| H | -1.84875900 | 0.85080900 | 1.65672500 |
| H | 2.88606100 | -0.69889000 | -0.95609600 |
| Cl | 2.17305400 | 1.29599200 | 0.08649000 |
| Cl | -2.62879000 | 0.63150900 | -0.55947200 |

## Agnostic Conformations of $XH_2C–S–S–CH_2X$

**Table S29.** X = Me

| | | | |
|---|---|---|---|
| C | -1.79142500 | 0.57525600 | -0.49567800 |
| C | 1.79142500 | 0.57525800 | 0.49567700 |
| S | 0.93070300 | -0.73379000 | -0.44870800 |
| S | -0.93070300 | -0.73379000 | 0.44870900 |
| H | 1.78225000 | 0.29426300 | 1.54863200 |
| H | -1.24125800 | 1.50966600 | -0.37763900 |
| H | 1.24125800 | 1.50966700 | 0.37763500 |
| H | -1.78225200 | 0.29425900 | -1.54863300 |
| C | -3.21384300 | 0.70813200 | 0.03253800 |
| H | -3.74732400 | 1.48184300 | -0.52271300 |
| H | -3.76225500 | -0.22906600 | -0.07909400 |
| H | -3.21796900 | 0.98360700 | 1.08879600 |
| C | 3.21384400 | 0.70813100 | -0.03253700 |
| H | 3.74732400 | 1.48184300 | 0.52271200 |
| H | 3.76225400 | -0.22906700 | 0.07909700 |
| H | 3.21797100 | 0.98360500 | -1.08879600 |

**Table S30.** X = OMe

| | | | |
|---|---|---|---|
| C | -1.79600400 | 0.18720600 | -0.33974600 |
| C | 1.79599600 | 0.18722300 | 0.33973100 |
| S | 0.85889100 | -1.09571100 | -0.57275900 |
| S | -0.85889200 | -1.09570700 | 0.57276700 |
| H | 2.02298300 | -0.18754200 | 1.34419700 |
| H | -1.18489500 | 1.09472000 | -0.41945300 |
| H | 1.18490200 | 1.09475100 | 0.41938000 |
| H | -2.02303300 | -0.18759600 | -1.34418900 |
| O | -2.95541700 | 0.40815400 | 0.40219600 |
| O | 2.95543900 | 0.40811900 | -0.40218000 |
| C | -3.84705100 | 1.28356500 | -0.25381900 |
| H | -4.71166700 | 1.40543000 | 0.39551500 |
| H | -3.38219500 | 2.26174000 | -0.42597300 |
| H | -4.16996400 | 0.86716800 | -1.21514500 |
| C | 3.84704500 | 1.28357700 | 0.25381100 |
| H | 4.16998800 | 0.86720900 | 1.21513900 |
| H | 4.71164700 | 1.40547000 | -0.39553600 |
| H | 3.38215000 | 2.26173500 | 0.42595600 |

**Table S31.** X = F

| | | | |
|---|---|---|---|
| C | 1.74023500 | 0.52493500 | 0.52840300 |
| C | -1.74023400 | 0.52493800 | -0.52840200 |
| S | -0.90633100 | -0.75336200 | 0.49391900 |
| S | 0.90633300 | -0.75336400 | -0.49391900 |
| H | -1.93028000 | 0.13290300 | -1.52644300 |
| H | 1.12829000 | 1.42584900 | 0.56848000 |
| H | -1.12829100 | 1.42585300 | -0.56847400 |
| H | 1.93028300 | 0.13289700 | 1.52644200 |
| F | 2.93365600 | 0.81616200 | -0.07357800 |
| F | -2.93365900 | 0.81615800 | 0.07357700 |

**Table S32.** X = Cl

| | | | |
|---|---|---|---|
| C | -1.73495600 | -0.37289900 | 0.57318300 |
| C | 1.73487400 | -0.37309200 | -0.57305500 |
| S | 0.92952600 | 0.91037800 | 0.44976000 |
| S | -0.92948300 | 0.91034600 | -0.44982700 |
| H | 1.80861500 | -0.03618600 | -1.60284900 |
| H | -1.18886000 | -1.31036200 | 0.51181300 |
| H | 1.18886400 | -1.31059000 | -0.51139900 |
| H | -1.80889200 | -0.03577300 | 1.60289200 |
| Cl | -3.37910000 | -0.64597800 | -0.04846800 |
| Cl | 3.37910500 | -0.64594700 | 0.04845800 |