Supporting information for article:

The susceptibility of disulfide bonds towards radiation damage may be explained by S···O interactions

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Table S1  Charges\(a\) on the S atom and the total energy\(b\) of the system (as calculated using Hartree-Fock theory with basis set 6-31++G(2d,2p)) at different values of \(\theta\) and \(\phi\), and S···O distance of 3.08 Å\(c\).

| \(\phi\) (°) | \(0\) (°)\(a\) | \(45\) | \(0\) |
|--------------|------------|------|------|
| -60\(b\)    | 0.0        | 0.63 | 5.02 |
|              | (-0.297, 0.005) | (-0.187, -0.063) | (-0.233, 0.066) |
| 0            | 0.94       | 3.89 |      |
|              | (-0.163, -0.084) | (-0.192, 0.038) |      |
| +50          | 0.31       | 2.01 |      |
|              | (-0.074, -0.070) | (-0.066, -0.158) |      |

\(a\) The charges on distant and neighboring S atoms (S\(_\gamma\)' and S\(_\gamma\), respectively) are given in parenthesis.

\(b\) \((\text{ERHF})\) (a.u) obtained from the program was first converted into kcal/mol. The value at a given \((\theta, \phi)\) was then expressed relative to that at \((90°, -60°)\), i.e., \(\Delta E = \text{ERHF}(\theta, \phi) - \text{ERHF}(90°, -60°)\).

\(c\) Calculations were also done at two distances on either side of 3.08 Å, and the resulting charges are: (-0.319, 0.014) at 2.9 Å and (-0.284, -0.001) at 3.2 Å.
Table S2  Charges on the S atoms and energy of interaction when the amide group is rotated about the C=O axis, keeping the disulphide moiety fixed (using DFT/B3LYP/6-31G++(2d,2p) level of theory).

| Position | Dihedral angle(°)\(a\) | Charge on distant S atom | Charge on proximal S atom |
|----------|--------------------------|--------------------------|--------------------------|
| 1        | -12                      | -0.155                   | 0.026                    |
| 2        | -42                      | -0.154                   | 0.019                    |
| 3        | -72                      | -0.151                   | -0.001                   |
| 4        | -102                     | -0.146                   | 0.001                    |
| 5        | -132                     | -0.142                   | -0.011                   |
| 6        | -162                     | -0.143                   | -0.002                   |
| 7        | -180(or +180)            | -0.139                   | -0.002                   |
| 8        | +150                     | -0.138                   | 0.016                    |
| 9        | +120                     | -0.151                   | 0.013                    |
| 10       | +90                      | -0.148                   | 0.001                    |
| 11       | +60                      | -0.151                   | 0.015                    |
| 12       | +30                      | -0.157                   | 0.031                    |
| 13       | 0                        | -0.157                   | 0.029                    |

\(a\) The virtual dihedral angle is defined by S\(_γ\)∙∙∙O-C-CH\(_3\). The position 1 corresponds to what is shown in Fig. 2.

Table S3  Second order perturbation theory analysis of the Fock matrix in NBO basis (using Hartree-Fock theory) of the model shown in Fig. 2 representing elastase.

| S\(_γ\)∙∙∙O distance (Å) | Donor (i) | Type | Acceptor (j) | Type | E(2)\(^a\) (kcal/mol) | \(\varepsilon(j)-\varepsilon(i)\)\(^b\) (a.u) |
|--------------------------|-----------|------|--------------|------|------------------------|---------------------------------|
| 2.9                      | O         | LP (1)| S\(_γ\)-S\(_γ'\) | σ*   | 1.42                   | 1.25                            |
|                          |           | LP (2)|              |      | 0.18                   | 0.72                            |
| 3.08                     | O         | LP (1)| S\(_γ\)-S\(_γ'\) | σ*   | 0.62                   | 1.25                            |
|                          |           | LP (2)|              |      | 0.08                   | 0.71                            |
| 3.2                      | O         | LP (1)| S\(_γ\)-S\(_γ'\) | σ*   | 0.35                   | 1.25                            |
|                          |           | LP (2)|              |      | 0.05                   | 0.71                            |

\(^a\) E(2) means energy of hyperconjugative interaction (stabilization energy). The default threshold of 0.05 kcal/mol was used.

\(^b\) Energy difference between donor (i) and acceptor (j) NBO orbitals.