ESI 1 Table S1 Molar absorbances, ε, for alkyl 4-nitrophenyl sulfides and sulfoxides at λ_{max} of the sulfide in acetone

R	λ_{max}/nm	ε_S/ m^2 mol^{-1}	ε_{SO}/ m^2 mol^{-1}
Me	342	1207.8 $\pm$ 11.3	104.1 $\pm$ 4.1
Et	342	1309.7 $\pm$ 10.1	186.8 $\pm$ 8.2
i-Pr	342	1179.6 $\pm$ 13.0	114.5 $\pm$ 6.6
n-Bu	344	1400.2 $\pm$ 13.8	154.1 $\pm$ 10.2
s-Bu	344	1306.0 $\pm$ 12.5	165.1 $\pm$ 11.6
t-Bu	338	379.5 $\pm$ 6.8	133.0 $\pm$ 7.5

ESI 2 Substituent constants for aliphatic hydrocarbon moieties

2.1 Alkyl groups

An early approach to the correlation of reactivities that vary as a result of alkyl group change was *via* the Taft-Pavelich equation[1] [eqn (S1)] (see end of ESI 2 for refs.). Here, $k(R)/k(Me)$ is a rate constant for a substrate bearing an alkyl group R relative to that of an analogous substrate bearing a methyl group, σ^* is a substituent constant measuring the inductive effect of R and E_s is a parameter measuring its steric effect; ρ^* and δ are the corresponding susceptibility constants appropriate to the reaction to which the equation is applied.

$$\log [k(R)/k(Me)] = \rho^*\sigma^* + \delta E_s \tag{S1}$$

The explanatory variables in eqn (S1) were respectively defined by eqn (S2) and eqn (S3):[1]

$$\sigma^* = \{\log [k(R)/k(Me)]_B - \log [k(R)/k(Me)]_A\}/2.48 \tag{S2}$$

$$E_s = \log [k(R)/k(Me)]_A \tag{S3}$$

where $[k(R)/k(Me)]_B$ is the rate constant of basic hydrolysis of esters RCO_2R' relative to that of $MeCO_2R'$ and $[k(R)/k(Me)]_A$ is the corresponding relative rate constant for acidic hydrolysis; the factor 2.48 adjusts the range of σ^* to values comparable with Hammett's aromatic substituent constants, σ_m and σ_p.[2]

The fitness for purpose of the σ^* scale, when applied to simple alkyl groups, as opposed to groups containing substituent heteroatoms, was questioned by various authors.[3–6] It was suggested that for simple alkyl groups the separation of inductive and steric effects fails and that Taft's σ^* values are artefacts and properly zero. Similar criticisms[7] were also advanced in respect of the σ_I values of simple alkyl groups initially derived[8a] from σ^* but also related to the protolytic equilibrium constants of α-substituted ethanoic acids[8b] and 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids[8c] and to ^{19}F chemical shifts in 3-substituted fluorobenzenes[8d,e] and which are referred to H rather than Me. The doubts concerning the reality of the σ^* and σ_I values for simple alkyl groups arose because they are small in comparison with the values for heteroatom-containing groups and are liable to masking by experimental error when determined by means of measurements in solution. These doubts were eventually dispelled by the finding by Levitt and co-workers[9] that, for numerous families of alkyl compound, RX, the differences in adiabatic first ionization energy, $E_I(RX)$, between particular

compounds and a chosen reference within the family, could be correlated by the solution-derived σ^* or σ_I scales, *e.g.* eqn (S4):

$$E_I(RX) - E_I(R_0X) = r(X)\sigma(R) \tag{S4}$$

in which $\sigma(R)$ is $\sigma^*(R)$ when R_0 is Me, or $\sigma_I(R)$ when R_0 is H, and $r(X)$ is the corresponding susceptibility constant $r^*(X)$ or $r_I(X)$. As gas-phase measurements of ionization energies are sensitive to variation in the alkyl group and are free of steric and solvent-dependent effects, Levitt and Widing scaled them to obtain accurate values of σ_I for common alkyl groups; they also noted relationships between the σ_I values within subsets of alkyl groups such as the linear (normal) subset or the α-branched subset.[9] Based upon their finding that for linear alkyl groups a plot of σ_I *versus n*, the number of carbon atoms in the chain, is a branch of a rectangular hyperbola, one of us[10] showed that the value of σ_I for any alkyl group could be calculated by use of eqn (S5),

$$\sigma_I = \frac{-1}{|\chi_H|} \times \sum_{i=1}^{i} \frac{n_i}{(4i^2 - 1)} \tag{S5}$$

where χ_H is the Mulliken electronegativity of hydrogen,[11] and n_i is the number of carbon atoms of *i*th type; thus, for example, for the 2-propyl group $\sigma_I = -0.1393 \times (1/3 + 2/15) = -0.0650$. The summation was termed the *connectivity characteristic* of the alkyl group and σ^* was found to be a function of the same characteristic [eqn (S6)],[10]

$$\sigma^* = 0.5 \times [1 - 3 \times \sum_{i=1}^{i} \frac{n_i}{(4i^2 - 1)}] \tag{S6}$$

Since the connectivity characteristic depends only on the catenation pattern it is independent of the bond-lengths, bond-angles and conformational factors which govern steric and solvation effects; the calculated substituent constants, whether of σ^* or σ_I, must therefore be free of any such influence.

An alternative approach to the calculation of unknown σ^* constants has been by extrapolation from known solution-derived values.[12] Although the method was primarily aimed at finding constants for complex groups or those containing heteroatoms, values were given for common alkyl groups [eqn (S7)]:

$$\sigma^*(R) = -\sigma^*(H) \times \sum_{i} (n_i \times a^i) \tag{S7}$$

where $\sigma^*(H) = 0.49$ (*cf.* Table S2), a is an empirical parameter: 0.202, and n_i enumerates carbon atoms of ith type from the α-position(s) [*n.b.* the difference from eqn (S6) in which i includes the *ipso* carbon atom]. The disadvantage of this procedure is that errors in the solution-derived experimental $\sigma^*(R)$ values used for calibration are propagated into the value of a and hence into calculated values of $\sigma^*(R)$. From the above, it is seen that there exist several sets of interrelated substituent constants σ of varied provenance that may be used for describing the inductive effects of alkyl groups (see Table S2).

Taft's steric substituent constant[1] E_s met with criticism[4] because he had included rate constants for esterification of RCO_2H and acidic alcoholysis of esters along with the acidic ester hydrolysis values used in eqn (S3). Dubois overcame this objection by introducing a new constant E_s' given by eqn (S8), in which the defining reaction is the methylation of RCO_2H in methanol catalysed by toluenesulfonic acid at 313 K.[13a] The range of E_S' extends over eight orders of magnitude and the constants have been used in the topological analysis of steric effects.[13b,c]

$$E_s' = \log [k(R)/k(Me)]_A \tag{S8}$$

Charton[14] also introduced a steric parameter (upsilon), υ, based on the van der Waals radius, $r_V/\text{Å}$, of a substituent group, X [eqn (S9)]. Such a definition is applicable only to monatomic X but for symmetric groups such as Me, t-Bu, CCl_3 and $SiMe_3$ a minimum van der Waals radius could be defined. Esterification rate constants for limited sets of these groups were correlated by eqn (S10) and the coefficients ψ and h so found were then used to evaluate υ constants from the esterification rate constants of less symmetrical groups.

$$\upsilon = r_V(X) - r_V(H) = r_V(X) - 1.20 \tag{S9}$$

$$\log k = \psi\upsilon + h \tag{S10}$$

The values of E_s and E_s' are comparable for many groups and, for all groups except H, they are ≤ 0 since all other groups are larger than (and therefore hinder reaction more than) the methyl group to which both scales are referred. By contrast, the values of υ are positive and are referred to H. There are thus three scales which measure steric effects of alkyl groups which are relevant to the present study (see Table S2).

Table S2 Comparison of substituent constants for alkyl groups

R	$-\sigma^*_{(T)}$ [a]	$-\sigma^*_{conn}$ [b]	$-\sigma^*_{(B)}$ [c]	$-\sigma_{I(T)}$ [d]	$-\sigma_{I(L)}$ [e]	$-\sigma_{Iconn}$ [b]	$-E_s$ [a]	$-E_s{}'$ [f]	υ [g]
H	−0.490	−0.5000	−0.490	0.000[h]	0.0000[h]	0.0000[h]	−1.24	−1.12	0.00[h]
Me	0.000[h]	0.0000[h]	0.000[h]	0.046	0.0460	0.0464	0.00[h]	0.00[h]	0.52
Et	0.100	0.1000	0.099	0.055	0.0560	0.0557	0.07	0.08	0.56
n-Pr	0.115	0.1429	0.119	0.057†	0.0607	0.0597	0.36	0.31	0.68
i-Pr	0.190	0.2000	0.198	0.064	0.0649	0.0650	0.47	0.48	0.76
n-Bu	0.130	0.1667	0.123	0.058†	0.0637	0.0619	0.39	0.31	0.68
i-Bu	0.125	0.1857	0.139	0.058†	0.0657	0.0637	0.93	0.93	0.98
s-Bu	0.210	0.2429	0.218	0.066†	0.0687	0.0690	1.13	1.00	1.02
t-Bu	0.300	0.3000	0.297	0.074	0.0743	0.0743	1.54	1.43	1.24
n-Pe	0.16[i]	0.1818	0.124	0.061†	0.0643	0.0633	0.40	0.31	0.68
i-Pe	0.16[j]	0.1905	0.143	0.061†		0.0641	0.35	0.32	0.68
neo-Pe	0.165	0.2286	0.159	0.062†		0.0677	1.74	1.63	1.34
Et₂CH	0.225	0.2857	0.238	0.067†		0.0730	1.98	2.00	1.51
t-Pe	0.310[k]	0.3429	0.317	0.075†		0.0783	2.17[k]	2.28	
n-Hx	0.16[j]	0.1923	0.124	0.061†		0.0643			0.73
t-Bu(Me)CH	0.280	0.3286	0.258	0.072†		0.0769	3.33	3.21	2.11

[a] Solution-derived values from R. W. Taft in ref. 1b except where otherwise indicated.

[b] Values calculated from group connectivity, see eqn (S5) and eqn (S6) (ref 10).

[c] Values interpolated from Taft's values for simpler groups, see eqn (S7) (ref. 12).

[d] Values for the α-branched set from R. W. Taft and I. C. Lewis in ref. 8b; otherwise (†) calculated from corresponding $\sigma^*_{(T)}$ via $\sigma_{I(T)} = -0.046 \times [1 - 2.04 \times \sigma^*_{(T)}]$ (ref. 9).

[e] Gas-phase, ionization energy-derived values from L. S. Levitt and H. F. Widing in ref. 9.

[f] Values obtained via the competitive methylation rates of carboxylic acids in methanol acidified with MeC₆H₄SO₃H (ref.13a).

[g] Values obtained via rates of acid- and base-catalysed ester hydrolyses calibrated by reference to the rates of symmetrical groups for which minimal van der Waals radii could be calculated (ref. 14).

[h] Values zero by definition.

[i] Value from A. B. Haefelmeyer and C. K. Hancock in ref 15.

[j] Value from H. Bock and G. Wagner in ref 16.

[k] Values from N. B. Chapman, J. R. Lee and J. Shorter in ref 17.

Table S3 Correlation analysis of the logarithms of the rate constants[a] for oxidations of alkyl 4-nitrophenyl sulfides by dimethyldioxirane in acetone at 291.3 K

Entry[c]	Substituent constants[b] Inductive	Steric	R^{2} [d]	F [e]	F_{signif} [f]	s [g]	ψ [h]	Intercept c [i]	ρ [i,j] / β_l [i]	δ [i,j] / β_s [i]	$|\beta_s/\beta_l|$ [k]
1 (i)	$\sigma_{I(L)}$	E_s	0.9787	68.94	3.11×10^{-3}	0.0127	0.206	2.274 ± 0.214	-10.166 ± 3.939	0.226 ± 0.065	
(ii)				91.92	2.03×10^{-3}	0.1631			-1.509 ± 0.444	2.054 ± 0.444	1.362 ± 0.179
2 (i)	σ_{Iconn}	E_s'	0.9648	41.09	6.61×10^{-3}	0.0163	0.265	2.215 ± 0.337	-11.360 ± 5.743	0.269 ± 0.102	
(ii)				54.79	4.35×10^{-3}	0.2098			-1.672 ± 0.639	2.234 ± 0.639	1.336 ± 0.230
3 (i)	σ^*_{conn}	E_s'	0.9648	41.09	6.61×10^{-3}	0.0163	0.265	2.742 ± 0.050	-1.055 ± 0.533	0.269 ± 0.102	
(ii)				54.79	4.35×10^{-3}	0.2098			-1.672 ± 0.639	2.234 ± 0.639	1.336 ± 0.230
4 (i)	$\sigma_{I(L)}$	υ	0.9640	40.18	6.83×10^{-3}	0.0165	0.268	2.532 ± 0.203	-10.128 ± 5.169	-0.490 ± 0.184	
(ii)				53.57	4.49×10^{-3}	0.2121			-1.504 ± 0.580	-2.045 ± 0.580	1.360 ± 0.234
5 (i)	$\sigma_{I(L)}$	E_s'	0.9636	39.70	6.95×10^{-3}	0.0166	0.270	2.281 ± 0.278	-10.050 ± 5.173	0.245 ± 0.092	
(ii)				52.93	4.58×10^{-3}	0.2133			-1.492 ± 0.580	2.034 ± 0.580	1.364 ± 0.237
6 (i)	σ_{Iconn}	υ	0.9620	38.00	7.40×10^{-3}	0.0169	0.276	2.492 ± 0.229	-11.391 ± 5.984	-0.536 ± 0.212	
(ii)				50.66	4.88×10^{-3}	0.2179			-1.677 ± 0.666	-2.238 ± 0.665	1.334 ± 0.238
7 (i)	σ^*_{conn}	υ	0.9620	38.00	7.40×10^{-3}	0.0169	0.276	3.021 ± 0.094	-1.058 ± 0.556	-0.536 ± 0.212	
(ii)				50.66	4.88×10^{-3}	0.2179			-1.677 ± 0.666	-2.238 ± 0.665	1.334 ± 0.238
8 (i)	σ_{Iconn}	E_s	0.9612	37.13	7.65×10^{-3}	0.0171	0.279	2.228 ± 0.318	-11.098 ± 5.947	0.242 ± 0.097	
(ii)				49.50	5.04×10^{-3}	0.2203			-1.634 ± 0.661	2.198 ± 0.662	1.345 ± 0.244
9 (i)	σ^*_{conn}	E_s	0.9612	37.13	7.65×10^{-3}	0.0171	0.279	2.744 ± 0.053	-1.031 ± 0.552	0.242 ± 0.097	
(ii)				49.50	5.04×10^{-3}	0.2203			-1.634 ± 0.662	2.198 ± 0.662	1.345 ± 0.244
10 (i)	$\sigma^*_{(T)}$	E_s'	0.9582	34.38	8.55×10^{-3}	0.0178	0.289	2.746 ± 0.053	-1.190 ± 0.660	0.288 ± 0.122	
(ii)				45.84	5.64×10^{-3}	0.2286			-1.819 ± 0.763	2.396 ± 0.762	1.317 ± 0.250
11 (i)	$\sigma^*_{(T)}$	υ	0.9534	30.71	1.00×10^{-2}	0.0187	0.305	3.045 ± 0.113	-1.189 ± 0.698	-0.574 ± 0.256	
(ii)				40.94	6.64×10^{-3}	0.2413			-1.818 ± 0.807	-2.394 ± 0.807	1.316 ± 0.264
12 (i)	$\sigma_{I(T)}$	E_s'	0.9501	28.58	1.11×10^{-2}	0.0194	0.316	2.161 ± 0.404	-12.733 ± 7.785	0.291 ± 0.135	
(ii)				38.11	7.37×10^{-3}	0.2497			-1.838 ± 0.849	2.418 ± 0.849	1.316 ± 0.275
13 (i)	$\sigma_{I(T)}$	υ	0.9442	25.38	1.31×10^{-2}	0.0205	0.334	2.464 ± 0.300	-12.7700 ± 8.246	-0.578 ± 0.285	
(ii)				33.85	8.74×10^{-3}	0.2641			-1.833 ± 0.899	-2.412 ± 0.899	1.316 ± 0.292
14 (i)	$\sigma^*_{(B)}$	E_s'	0.9253	18.59	2.04×10^{-2}	0.0237	0.386	2.750 ± 0.070	-1.121 ± 0.862	0.278 ± 0.161	
(ii)				24.78	1.36×10^{-2}	0.3055			-1.733 ± 1.008	2.313 ± 1.008	1.334 ± 0.349
15 (i)	$\sigma^*_{(B)}$	υ	0.9171	16.59	2.39×10^{-2}	0.0250	0.407	3.037 ± 0.151	-1.112 ± 0.908	-0.551 ± 0.337	
(ii)				22.13	1.60×10^{-2}	0.3219			-1.556 ± 1.061	-2.299 ± 1.061	1.336 ± 0.371
16 (i)	$\sigma^*_{(T)}$	E_s	0.8895	12.08	3.67×10^{-2}	0.0289	0.470	2.755 ± 0.083	-1.017 ± 1.002	0.235 ± 0.169	
(ii)				16.11	2.49×10^{-2}	0.3720			-1.556 ± 1.157	2.137 ± 1.158	1.374 ± 0.455
17 (i)	$\sigma_{I(T)}$	E_s	0.8811	11.12	4.10×10^{-2}	0.0300	0.488	2.258 ± 0.582	-10.844 ± 11.198	0.237 ± 0.178	
(ii)				14.82	2.79×10^{-2}	0.3855			-1.565 ± 1.221	2.150 ± 1.221	1.374 ± 0.477
18 (i)	$\sigma^*_{(B)}$	E_s	0.8557	8.89	5.48×10^{-2}	0.0330	0.537	2.760 ± 0.093	-0.945 ± 1.114	0.225 ± 0.190	
(ii)				11.66	3.76×10^{-2}	0.4247			-1.462 ± 1.302	2.047 ± 1.302	1.400 ± 0.552

Footnotes to Table S3

^{a} No. of data points is 6. ^{b} For identification see Table S2. ^{c} (i) Results of correlation using raw substituent constants; (ii) results using standardised variables. ^{d} R is the correlation coefficient; entries are ordered as decreasing values of R. ^{e} $F = R^2(n - m)/[(1 - R^2)(m - 1)]$ where $(m - 1)$ is the no. of explanatory variables. ^{f} The smaller the value of F_{signif}, the greater is the significance level of the regression. ^{g} The standard error of the estimate. ^{h} $\psi = [n(1 - R^2)/(n - m)]^{1/2}$; $\psi < 0.02$, very good; $0.02 < \psi < 0.1$, good; $0.1 < \psi < 0.2$, fair; $0.2 < \psi < 0.5$, poor (*cf.* Exner ref. 18). On this criterion, the present correlations are 'poor', probably as a result of the small data set]. ^{i} The uncertainties on the intercepts and regression coefficients are the 95% confidence intervals. ^{j} ρ and δ are retained for non-standardised regressions although the variables may be referred to different standards, H or Me. ^{k} The uncertainties on $|\beta_s/\beta_l|$ are standard errors.

Comments on Table S3

In the most precise correlation (entry 1), it is not surprising to find Levitt and Widing's refined measure of alkyl inductive effects,^{9} $\sigma_{I(L)}$, as the statistically preferred inductive substituent constant but it is surprising to find it paired with the flawed steric constant, E_s, rather than the improved $E_s{}'$. This presumably arises from a fortuitous cancellation of errors. All of the other σ constants, including those derived from $\sigma_{I(L)}$ *via* the group connectivity, pair with the three steric constants in the preferred order $E_s{}' > \upsilon > E_s$.

The second most precise pairing of substituent constants (entries 2 and 3) is found for either σ^*_{conn} or σ_{Iconn} paired with $E_s{}'$; indeed, with any steric partner in common (entries 6 and 7, 8 and 9), they give identical goodness-of-fit statistics (intercepts and regression coefficients differ, of course). Both are functions of the same connectivity characteristic and the goodness-of-fit statistics are clearly independent of any factor which multiplies it. Eqn (S6) reproduces well the $\sigma^*_{(T)}$ values of the α-branched subset of alkyl groups but it somewhat overestimates $\sigma^*(H)_{(T)}$ and the values for other alkyl groups (see Table S2). Replacement of the initial factor of 0.5 in eqn. (S6) by 0.49 to correct prediction of $\sigma^*(H)_{(T)}$ or variation of the factors 0.5 and 3 to 0.486 and 2.899, respectively, to reproduce the least squares fit of $\sigma^*_{(T)}$ to the connectivity characteristic would therefore not improve the goodness-of-fit statistics.

2.2 The inductive effect of the polymethylene chain in saturated mono-heterocycles

If it is assumed that the inductive effect of the polymethylene chain in a saturated mono-heterocycle varies smoothly with chain-length as a branch of a rectangular hyperbola, as does that of linear alkyl groups then, from the work of Levitt and Widing,[9] it is expected that the gas-phase adiabatic first ionization energies $E_I(x)_Z$ of x-membered mono-heterocycles with heteroatom Z should be given by eqn (S11):

$$E_I(x)_Z = E_I(\infty)_Z \frac{x}{(x - b)} \tag{S11}$$

where $E_I(\infty)_Z$ is the ionization energy of a notional heterocycle of infinite ring-size and b is a constant.

Rearrangement of eqn (S11) gives eqn (S12),

$$\frac{x}{E_I(x)_Z} = \frac{x}{E_I(\infty)_Z} - \frac{b}{E_I(\infty)_Z} \tag{S12}$$

and a plot of $x/E_I(x)_Z$ vs x is expected to be linear with gradient $1/E_I(\infty)_Z$ and intercept $-b/E_I(\infty)_Z$. Data for $(CH_2)_nO$, $(CH_2)_nNH$, $(CH_2)_nS$, and $(CH_2)_nSO$ [see Table S4(a)] do plot linearly, confirming a hyperbolic relationship in each case but the plots show heteroatom-dependent differences of gradient and intercept. These can be reduced by division of $E_I(x)_Z$ by the value of the corresponding 3-membered ring [giving $E_I(x)_{Zrel(3)}$] which allows cancellation of $E_I(\infty)_Z$ [as $E_I(3)_Z = E_I(\infty)_Z \times 3/(3 - b)$, $cf.$ eqn (S11)]; eqn (S12) then becomes,
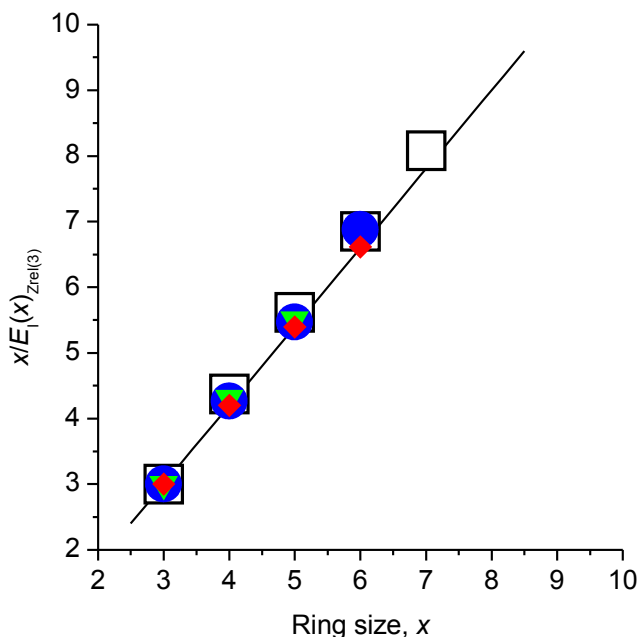
$$\frac{x}{E_I(x)_{Zrel(3)}} = \frac{xE_I(3)_Z}{E_I(\infty)_Z} - \frac{bE_I(3)_Z}{E_I(\infty)_Z} = \frac{3x}{(3 - b)} - \frac{3b}{(3 - b)} \tag{S13}$$

Fig. S1 shows the plots of $x/E_I(x)_{Zrel(3)}$ vs x for the four sets of heterocycles relative to the line having gradient 1.2 and intercept -0.6. The agreement suggests a common value of $b = 0.5$.

Eqn (S11) then becomes,

$$E_I(x)_Z = E_I(\infty)_Z \frac{x}{(x - 0.5)} \equiv 2E_I(\infty)_Z \frac{x}{(2x - 1)} \tag{S14}$$

Fig. S1 Variation of $x/E_I(x)_{Zrel(3)}$ with ring size, x, for heterocycles $(CH_2)_nZ$. Squares, $Z = O$; blue circles, $Z = NH$; green triangles, $Z = SO$; red diamonds, $Z = S$. The line has gradient 1.2 and intercept -0.6.

Values of $E_I(\infty)_O$, $E_I(\infty)_{NH}$, $E_I(\infty)_S$, and $E_I(\infty)_{SO}$ are found to be 8.35, 7.18, 7.51 and 7.70 eV, respectively, from the gradients of the plots of $x/E_I(x)$ vs x but these values cannot, in general, be used in eqn (S14) to express $E_I(x)_Z$ adequately since each has an associated value of b which is somewhat different from 0.5 (0.5–0.7); the fortuitous exception is $E_I(\infty)_S$. Alternatively, if values of $E_I(\infty)_Z$ are found from eqn (S14), they are essentially constant for $x > 3$ but a somewhat larger value results for $x = 3$ in the case of the electronegative hetero-functions O and SO. Values of $E_I(\infty)_O$, $E_I(\infty)_{NH}$, $E_I(\infty)_S$, and $E_I(\infty)_{SO}$ found from eqn (S14) for $x > 3$ are, respectively, 8.47, 7.54, 7.53 and 7.87 eV.

Notwithstanding the uncertainty in specifying $E_I(\infty)_Z$ for a common value of b, we note that for a mono-heterocycle, $x = (n + 1)$ where n is the number of C atoms; substitution in eqn (S14) gives,

$$E_I(x)_Z = 2E_I(\infty)_Z \frac{(n+1)}{(2n+1)} \tag{S15}$$

The change to $E_I(x)_Z$ on adding the ith C atom is thus:

$$\Delta E_I(x)_Z = 2E_I(\infty)_Z \left\{ \frac{(i+1)}{(2i+1)} - \frac{[(i-1)+1]}{[2(i-1)+1]} \right\} = 2E_I(\infty)_Z \left\{ \frac{(i+1)(2i-1) - [i(2i+1)]}{(2i+1)(2i-1)} \right\} = \frac{-2E_I(\infty)_Z}{(4i^2 - 1)}$$

Hence, summing over all i,

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$$E_I(x)_Z = E_I(\infty)_Z \times \sum_{i=0}^{n} \frac{-2}{(4i^2 - 1)} \tag{S16}$$

Fig. S2 shows $E_I(x)_S$ and $E_I(x)_{SO}$, calculated *via* eqn (S16) with 7.53 eV and 7.87 eV, respectively, for $E_I(\infty)_Z$ (see Table S5), plotted *versus* their experimental values [see Table S4(*i*)]; the line has unit gradient. It is clear the equation reproduces well, in terms of connectivity, the data from which it is derived.
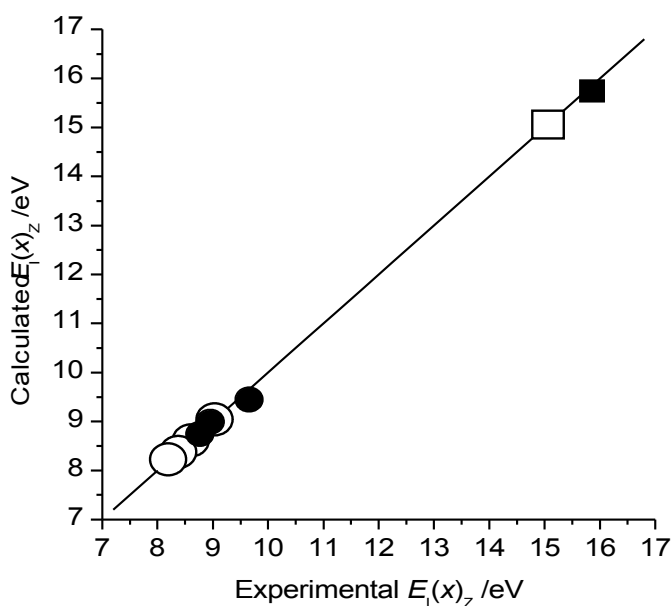
Fig. S2 Plot of calculated *versus* experimental ionization energies. Open circles, sulfides; filled circles, sulfoxides. The open and filled squares are the corresponding $2E_I(\infty)_Z$ values.

Although a mono-heterocycle must have at least two C atoms, the summation in eqn (S16) runs from $i = 0$ to n; thus in thiirane, for example, the two equivalent C atoms each contribute to the connectivity effect on $E_I(x)_S$ as both the first and the second atom in the chain (equivalent to counting from S in both clockwise and anticlockwise senses). The effect of the connectivity of $-CH_2CH_2-$ in thiirane is thus as two ethyl groups and not two methyl groups and that for $-CH_2CH_2CH_2-$ in thietane is as two *n*-propyl groups and so forth. It is therefore possible to assign $\Sigma\sigma_I(n)$ and $\Sigma\sigma^*(n)$ values to the various lengths of polymethylene chain, *e.g.* $\Sigma\sigma_{Iconn}(2) = \Sigma\sigma_{Iconn}(Et)_2$ and $\Sigma\sigma^*_{conn}(3) = \Sigma\sigma^*_{conn}(n\text{-Pr})_2$ [see Table S5]. Since these substituent constants for the polymethylene chain have been obtained in terms of the connectivity, it seems sensible to relate them to similarly found alkyl substituent constants and to distinguish them by *n*, the number of carbon atoms contained (albeit when used in describing a property labelled by the ring size, *x*); it also seems sensible to use the $\Sigma\sigma*$ format on account of the

two attachments of the chain to the heteroatom comparable with the attachment of two equivalent alkyl groups.

When $E_I(R_2S)$ and $E_I(x)_S$ with $E_I(R_2SO)$ and $E_I(x)_{SO}$ (see Table S4) are plotted versus $\Sigma\sigma^*_{conn}(R)_2$ calculated *via* eqn (S6) (see also Table S2) and $\Sigma\sigma^*_{conn}(n)$, two pairs of essentially parallel lines result (Fig. S3). These are given by eqn (S17) – (S20),

$$E_I(R_2S)/eV = (1.710 \pm 0.087)\Sigma\sigma^*_{conn}(R)_2 + (8.743 \pm 0.037) \tag{S17}$$

$R^2 = 0.9974$, $F = 2274.5$, $F_{sig} = 5.70 \times 10^{-9}$, $s = 0.043$, $\psi = 0.059$;

$$E_I(x)_S/eV = (4.989 \pm 0.034)\Sigma\sigma^*_{conn}(n) + (10.032 \pm 0.018) \tag{S18}$$

$R^2 = 1.000$, $F = 209353$, $F_{sig} = 2.30 \times 10^{-8}$, $s = 0.013$, $\psi = 0.005$;

$$E_I(R_2SO)/eV = (1.705 \pm 0.369)\Sigma\sigma^*_{conn}(R)_2 + (9.091 \pm 0.116) \tag{S19}$$

$R^2 = 0.9656$, $F = 140.55$, $F_{sig} = 7.52 \times 10^{-5}$, $s = 0.070$, $\psi = 0.219$;

$$E_I(x)_{SO}/eV = (4.947 \pm 0.577)\Sigma\sigma^*_{conn}(n) + (10.476 \pm 0.320) \tag{S20}$$

$R^2 = 0.9985$, $F = 1362.7$, $F_{sig} = 7.33 \times 10^{-4}$, $s = 0.148$, $\psi = 0.054$.
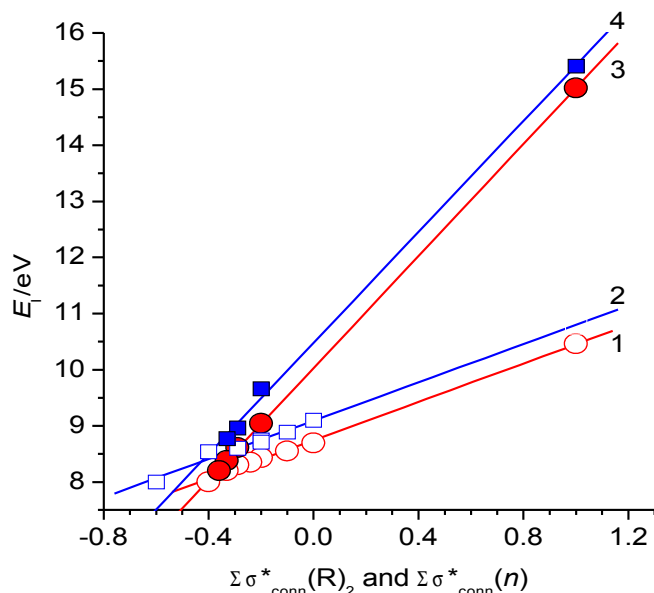
Fig. S3 Variation of $E_I(R_2S)$ and $E_I(R_2SO)$ with $\Sigma\sigma^*_{conn}(R)_2$ and of $E_I(x)_S$ and $E_I(x)_{SO}$ with $\Sigma\sigma^*_{conn}(n)$. Plot 1 (red open circles) dialkyl sulfides; plot 2 (blue open squares) dialkyl sulfoxides; plot 3 (red filled circles) cyclic sulfides; plot 4 (blue filled squares) cyclic sulfoxides.

Comparisons of eqn (S17) with eqn (S19) and of eqn (S18) with eqn (S20) show that the sulfoxides, whether acyclic or cyclic, have ionization energies which are about 0.4 eV higher than those of the

corresponding sulfides. Comparisons of eqn (S17) with eqn (S18) and of eqn (S19) with eqn (S20) show there is a ring-size effect on $E_I(x)$, additional to that produced by the variation in the polymethylene chain-length, which is more marked the smaller the ring. This surely arises from changes in the electronegativity of the orbitals of the all the ring atoms as their bonding geometry is constrained but particularly that of the hetero-function providing the orbital ionised. Effective substituent constants, $\Sigma\sigma^*_{eff}(n)_S$, for the polymethylene chain in cyclic sulfides having 3 to 8-membered rings, which are commensurate with those of the acyclic sulfides, are obtained from eqn (S17) and eqn (S18) *via* eqn (S21) (see Table S5),

$$\Sigma\sigma^*_{eff}(n)_S = \{(4.989 \pm 0.034)\Sigma\sigma^*_{conn}(n) + [(10.032 \pm 0.018) - (8.743 \pm 0.037)]\}/(1.710 \pm 0.087)$$
$$= (2.918 \pm 0.150)\Sigma\sigma^*_{conn}(n) + (0.754 \pm 0.045) \qquad (S21)$$

Likewise, for the cyclic sulfoxides effective substituent constants, $\Sigma\sigma^*_{eff}(n)_{SO}$, commensurate with those of acyclic sulfoxides are found *via* eqn (S22),

$$\Sigma\sigma^*_{eff}(n)_{SO} = \{(4.947 \pm 0.577)\Sigma\sigma^*_{conn}(n) + [(10.476 \pm 0.320) - (9.091 \pm 0.116)]\}/(1.705 \pm 0.369)$$
$$= (2.901 \pm 0.713)\Sigma\sigma^*_{conn}(n) + (0.812 \pm 0.266) \qquad (S22)$$

Comparison of eqn (S21) with eqn (S22) indicates a single equation [eqn (S23)] to apply to both sulfides and sulfoxides,

$$\Sigma\sigma^*_{eff}(n) = 2.91\Sigma\sigma^*_{conn}(n) + 0.78 \equiv 2.91\Sigma\sigma^*_{conn}[C_nH_{(2n+1)}]_2 + 0.78 \qquad (S23)$$

where the alkyl group $C_nH_{(2n+1)}$ is linear. Although there are differences in geometry between cyclic sulfides and sulfoxides of the same ring-size, as S is the atom which bridges the termini of the polymethylene chain in both cases, the differences must be sufficiently small to permit a particular length of chain to exert the same inductive effect on the ionization process in each case. From this it may be inferred that a similar situation holds in other electrophilic processes such as the oxidation of cyclic sulfides and sulfoxides by dimethyldioxirane. Values of $\Sigma\sigma^*_{eff}(n)$ are given in Table S5.

2.3 The steric effect of the polymethylene chain in saturated mono-heterocycles

Dubois and co-workers[13a] give $E_s'(Et) = -0.08$ then $E_s'(R) = -0.31$ for *n*-Pr, *n*-Bu, *n*-Pe; similarly, Charton[14] reported a common value of 0.68 for his steric constant, υ, for several linear alkyl groups, $C_nH_{(2n+1)}$, having *n* between 3 and 17. The simple rationale for the constancy of the steric substituent constants is that the alkyl chains can rotate to present essentially the same short length of polymethylene chain immediately adjacent to a reaction site. Although the conformational freedom of the polymethylene chain in saturated mono-heterocycles is restricted relative to that of alkyl chain, the

ring structure achieves a similar effect to alkyl chain rotation. It is likely that, the smaller the ring, the more effectively will the polymethylene chain be held away from a reaction centre at the heteroatom but, for the purpose of correlation, we shall assume that the two arms of polymethylene chain in the heterocycles of present interest exert a steric effect $\Sigma E_s' = 2 \times E_s'(R)$ where R is the linear alkyl group having the same number of C atoms as the heterocycle. Thus for the 3-membered rings $\Sigma E_s' = 2 \times E_s'$ (Et) $= 2 \times (-0.08) = -0.16$ and for the remainder $\Sigma E_s' = 2 \times (-0.31) = -0.62$.

Table S4 Selected first ionization energies[a]

(i) Mono-heterocycles

	$E_I(x)_Z$/eV							
Ring size, x	$(CH_2)_nO$	Ref.	$(CH_2)_nNH$	Ref.	$(CH_2)_nS$	Ref.	$(CH_2)_nSO$	Ref.
3	10.56	19	9.2	21	9.04	19	9.66^b	25
4	9.65	19	8.63	22	8.61	19	8.96^b	26
5	9.40	19	8.41	23	8.38	19	8.77^b	25
6	9.25	19	8.03	19	8.2	24		
7	9.15	20						

(ii) Dialkyl sulfides and sulfoxides

R	R′	$E_I(R_2S)$/eV	Ref.	$E_I(R_2SO)$/eV	Ref.
H	H	10.46	19		
Me	Me	8.69	19	9.10	31
Et	Me	8.55	19	8.89^c	32
i-Pr	Me			8.71^c	32
Et	Et	8.42	19	8.75	19
n-Pr	Et	8.37	27		
n-Pr	n-Pr	8.30	28	8.60^b	25
n-Bu	n-Bu	8.2	29		
i-Pr	i-Pr	8.0^d	30	8.54^c	32
t-Bu	t-Bu			8.0	25

[a] Data from ref. 19 are NIST 'evaluated' adiabatic ionization energies which, with one exception, have been used by preference when available; other preferred values were obtained *via* photo-ionization or photoelectron spectroscopy except where otherwise indicated. [b] Vertical ionization energy. [c] Obtained by electron impact. [d] Selected in preference to an 'evaluated' energy of 8.2 eV.

Table S5 Substituent constants and ionization energies calculated for cyclic sulfides and sulfoxides

	Polymethylene moiety				$(CH_2)_nS$	$(CH_2)_nSO$
Ring-size, x	C number, n	R_2 equivalent	$\Sigma\sigma^*_{conn}(n)^a$	$\Sigma\sigma^*_{eff}(n)^b$	$E_I(x)_{Scalc}$/eV^c	$E_I(x)_{SOcalc}$/eV^d
[1]	[0]				[15.06]	[15.74]
[2]	[1]				[10.04]	[10.49]
3	2	$(Et)_2$	−0.20	+0.20	9.04 $(9.04)^e$	9.44 $(9.66)^e$
4	3	$(n$-Pr$)_2$	−0.29	−0.05	8.61 $(8.61)^e$	8.99 $(8.96)^e$
5	4	$(n$-Bu$)_2$	−0.33	−0.19	8.37 $(8.38)^e$	8.74 $(8.77)^e$
6	5	$(n$-Pe$)_2$	−0.36	−0.28	8.21 $(8.2)^e$	8.59
7	6	$(n$-Hx$)_2$	−0.38	−0.34	8.11	8.48
8	7	$(n$-Hp$)_2$	−0.40	−0.38	8.03	8.39

[a] Calculated as the equivalent $\Sigma\sigma^*_{conn}(R)_2 = [1-3\times\Sigma 1/(4i^2-1)]$, *cf.* eqn. (S6). [b] Calculated *via* eqn (S23). [c] Calculated *via* eqn (S16) with $E_I(\infty)_S = 7.53$ eV. [d] Calculated *via* eqn (S16) with $E_I(\infty)_{SO} = 7.87$ eV. [e] Experimental values in parentheses, *cf.* Table S4(*i*).

Table S6 Parameters for overall correlation of reactivity

Substrate	log[k_2/dm^3 mol^{-1} s^{-1}]	Σσ*	q_S/e [a]	Φ/eV^{-1} [a]	$c^2_{S H}$ [a]	ΣE_s'	ΔE_{rs}/kJ mol^{-1}
4-MeOPhSMe	3.575 [b]	0.36 [c]	0.127	−0.2101	0.219	−2.31 [d]	0
4-MePhSMe	3.500 [b]	0.46 [c]	0.130	−0.1998	0.271	−2.31 [d]	0
PhSMe	3.371 [b]	0.60 [c]	0.132	−0.1941	0.293	−2.31 [d]	0
4-ClPhSMe	3.199 [b]	0.75 [c]	0.143	−0.1878	0.268	−2.31 [d]	0
4-NCPhSMe	2.872 [b]	1.05 [c]	0.160	−0.1744	0.283	−2.31 [d]	0
4-O$_2$NPhSMe	2.782 [b]	1.14 [c]	0.167	−0.1689	0.309	−2.31 [d]	0
3-MeOPhSMe	3.281 [b]	0.66 [c]	0.133	−0.1981	0.244	−2.31 [d]	0
3-ClPhSMe	3.090 [b]	0.85 [c]	0.147	−0.1839	0.292	−2.31 [d]	0
3-F$_3$CPhSMe	3.045 [b]	0.89 [c]	0.146	−0.1807	0.312	−2.31 [d]	0
3-NCPhSMe	2.848 [b]	0.92 [c]	0.154	−0.1746	0.314	−2.31 [d]	0
3-O$_2$NPhSMe	2.834 [b]	1.09 [c]	0.154	−0.1728	0.324	−2.31 [d]	0
4-MeOPhSOMe	1.666 [b]	0.36 [c]	0.762	−0.1855	0.062	−2.31 [d]	0
4-MePhSOMe	1.588 [b]	0.46 [c]	0.763	−0.1807	0.078	−2.31 [d]	0
PhSOMe	1.456 [b]	0.60 [c]	0.765	−0.1777	0.082	−2.31 [d]	0
4-ClPhSOMe	1.276 [b]	0.75 [c]	0.771	−0.1718	0.078	−2.31 [d]	0
4-NCPhSOMe	0.942 [b]	1.05 [c]	0.778	−0.1636	0.081	−2.31 [d]	0
4-O$_2$NPhSOMe	0.849 [b]	1.14 [c]	0.780	−0.1615	0.077	−2.31 [d]	0
3-MeOPhSOMe	1.362 [b]	0.66 [c]	0.766	−0.1811	0.046	−2.31 [d]	0
3-ClPhSOMe	1.167 [b]	0.85 [c]	0.774	−0.1703	0.078	−2.31 [d]	0
3-F$_3$CPhSOMe	1.121 [b]	0.89 [c]	0.776	−0.1687	0.077	−2.31 [d]	0
3-NCPhSOMe	1.021 [b]	0.92 [c]	0.781	−0.1639	0.053	−2.31 [d]	0
3-O$_2$NPhSOMe	0.903 [b]	1.09 [c]	0.785	−0.1629	0.077	−2.31 [d]	0
4-O$_2$NPhSMe	2.736 [e]	1.14 [c]	0.167	−0.1689	0.309	−2.31 [d]	0
4-O$_2$NPhSEt	2.844 [e]	1.04 [c]	0.167 [f]	−0.1689 [f]	0.309 [f]	−2.39 [d]	0
4-O$_2$NPhS(i-Pr)	2.816 [e]	0.94 [c]	0.167 [f]	−0.1689 [f]	0.309 [f]	−2.80 [d]	0
4-O$_2$NPhS(n-Bu)	2.779 [e]	0.97 [c]	0.167 [f]	−0.1689 [f]	0.309 [f]	−2.62 [d]	0
4-O$_2$NPhS(s-Bu)	2.715 [e]	0.90 [c]	0.167 [f]	−0.1689 [f]	0.309 [f]	−3.31 [d]	0
4-O$_2$NPhS(t-Bu)	2.687 [e]	0.84 [c]	0.167 [f]	−0.1689 [f]	0.309 [f]	−3.74 [d]	0
4-O$_2$NPhSOMe	0.919 [g]	1.14 [c]	0.780	−0.1615	0.077	−2.31 [d]	0
4-O$_2$NPhSOEt	1.107 [g]	1.04 [c]	0.780 [h]	−0.1615 [h]	0.077 [h]	−2.39 [d]	0
4-O$_2$NPhSO(n-Bu)	1.053 [g]	0.97 [c]	0.780 [h]	−0.1615 [h]	0.077 [h]	−2.62 [d]	0
4-O$_2$NPhSO(s-Bu)	1.079 [g]	0.90 [c]	0.780 [h]	−0.1615 [h]	0.077 [h]	−3.31 [d]	0
4-O$_2$NPhSO(t-Bu)	1.312 [g]	0.84 [c]	0.780 [h]	−0.1615 [h]	0.077 [h]	−3.74 [d]	0
(n-Pr)$_2$S	4.425 [i]	−0.29	0.077	−0.1890	0.457	−0.62	0
(t-Bu)$_2$S	3.827 [i]	−0.60	0.050	−0.1909	0.453	−2.86	0
(n-Pr)$_2$SO	2.114 [i]	−0.29	0.761	−0.1855	0.095	−0.62	0
(t-Bu)$_2$SO	2.582 [i]	−0.60	0.753	−0.1933	0.116	−2.86	0
(CH$_2$)$_2$S	3.375 [i]	0.20 [j]	−0.018	−0.1767	0.477	−0.16 [k]	12.8 [l]
(CH$_2$)$_3$S	4.137 [i]	−0.05 [j]	0.060	−0.1841	0.442	−0.62 [k]	−8.4 [l]
(CH$_2$)$_4$S	4.461 [i]	−0.19 [j]	0.057	−0.1896	0.452	−0.62 [k]	9.0 [l]
(CH$_2$)$_5$S	4.228 [i]	−0.28 [j]	0.073	−0.1874	0.356	−0.62 [k]	5.2 [l]
(CH$_2$)$_6$S	4.225 [i]	−0.34 [j]	0.068	−0.1887	0.368	−0.62 [k]	5.0 [l]
(CH$_2$)$_7$S	4.592 [i]	−0.38 [j]	0.073	−0.1899	0.172	−0.62 [k]	10.1 [l]
(CH$_2$)$_2$SO	1.149 [i]	0.20 [j]	0.678	−0.1658	0.059	−0.16 [k]	93.8 [m]
(CH$_2$)$_3$SO	1.281 [i]	−0.05 [j]	0.730	−0.1792	0.114	−0.62 [k]	15.2 [m]
(CH$_2$)$_4$SO	1.476 [i]	−0.19 [j]	0.760	−0.1842	0.068	−0.62 [k]	8.9 [m]
(CH$_2$)$_5$SO	1.919 [i]	−0.28 [j]	0.748	−0.1848	0.108	−0.62 [k]	−0.8 [m]
(CH$_2$)$_6$SO	2.297 [i]	−0.34 [j]	0.743	−0.1872	0.104	−0.62 [k]	−6.3 [m]
(CH$_2$)$_7$SO	2.316 [i]	−0.38 [j]	0.764	−0.1895	0.104	−0.62 [k]	−10.4 [m]

[a] Calculated in this work (see main text). [b] k_2 value at 293 K given in Table 7 of ref. 34b. [c] σ*(Ar) calculated by ACD algorithm (ref. 35), for σ*(R) see σ*$_{conn}$(R) in Table S2. [d] E_s' for 3- and 4-substituted phenyl assumed equal to E_s'(Ph) (*i.e.* the corollary of Hammett's assumption that only *ortho* substituents exert a steric effect on a side-chain attached at the *ipso* position); E_s' values from ref. 13a unless otherwise indicated. [e] k_2 value at 291.3 K given in Table 1. [f] Value assumed equal to that of 4-O$_2$NPhSMe. [g] k_2 value at 294.6 K given in Table 1. [h] Value assumed equal to that of 4-O$_2$NPhSOMe. [i] k_2 value at 293 K given in Table 4. [j] Effective value for the polymethylene chain, Σσ*$_{eff}$(n) (see ESI 2.2 and Table S5). [k] ΣE_s' value assumed equal to 2×E_s'(R) where R is the linear alkyl group with the same number of carbon atoms (see ESI 2.3) [l] ΔE_{rs}(I) from Table 8 (main text). [m] ΔE_{rs}(II) from Table 8 (main text).

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Table S7 Statistical comparison of equations (13) – (19) in the main text

Eqn		n^a	$R^{2\,b}$	F^c	$F_{signif}{}^d$	s^e	ψ^f	Intercept^g	Regression coefficients for the indicated variables:^{g}				
									q_S/e	$\Sigma\sigma^*$	$\Sigma E_s'$	Φ/eV^{-1}	ΔE_{rs}
(13)	(i)^h	5	0.9790	139.7	1.30×10^{-3}	0.079	0.187	1.915 ± 0.114	–	–	–	–	-0.0439 ± 0.0118
(14)	(i)^h	22	0.9995	19473	3.44×10^{-32}	0.024	0.024	4.336 ± 0.039	-3.061 ± 0.034	-0.949 ± 0.043	–	–	–
	(ii)			20498	2.11×10^{-32}	0.023		–	-0.965 ± 0.010	-0.233 ± 0.010	–	–	–
	(iii)							–	80.6	19.4	–	–	–
(15)	(i)^h	25	0.9987	8683.6	1.33×10^{-32}	0.039	0.038	4.324 ± 0.038	-3.056 ± 0.052	-0.922 ± 0.036	–	–	–
	(ii)			9078.3	8.16×10^{-33}	0.036		–	-0.942 ± 0.015	-0.403 ± 0.015	–	–	–
	(iii)							–	70.0	30.0	–	–	–
(16)	(i)^h	24	0.9857	460.1	1.30×10^{-18}	0.083	0.131	2.991 ± 0.721	–	-0.648 ± 0.101	0.289 ± 0.055	-7.190 ± 3.803	–
	(ii)			483.1	8.03×10^{-19}	0.125		–	–	-0.580 ± 0.088	0.408 ± 0.076	-0.133 ± 0.068	–
	(iii)							–	–	51.7	36.4	11.9	–
(17)	(i)^h	21	0.9909	618.6	1.50×10^{-17}	0.053	0.106	1.857 ± 0.075	–	-0.967 ± 0.058	-0.0576 ± 0.0389	–	-0.0056 ± 0.0014
	(ii)			655.0	9.27×10^{-18}	0.100		–	–	-1.035 ± 0.059	-0.0996 ± 0.0652	–	-0.226 ± 0.054
	(iii)								–	76.1	7.3	–	16.6
(18)	(i)^h	44	0.9919	1626.7	8.15×10^{-42}	0.107	0.095	4.287 ± 0.063	-3.027 ± 0.103	-0.928 ± 0.062	–	–	-0.0089 ± 0.0023
	(ii)			1667.4	4.99×10^{-42}	0.092		–	-0.850 ± 0.029	-0.435 ± 0.029	–	–	-0.111 ± 0.029
	(iii)								60.9	31.2	–	–	7.9
(19)	(i)^h	45	0.9849	652.1	7.89×10^{-36}	0.149	0.130	4.375 ± 0.137	-2.961 ± 0.142	-0.753 ± 0.107	0.110 ± 0.071	–	-0.0103 ± 0.0034
	(ii)			668.4	4.85×10^{-36}	0.127		–	-0.831 ± 0.039	-0.365 ± 0.051	0.0851 ± 0.0540	–	-0.127 ± 0.042
	(iii)								59.0	25.9	6.0	–	9.0

^{a} No. of data points. ^{b} R is the correlation coefficient. ^{c} $F = R^2(n-m)/[(1-R^2)(m-1)]$ where $(m-1)$ is the no. of explanatory variables. ^{d} The smaller the value of F_{signif}, the greater is the significance level of the regression. ^{e} The standard error of the estimate. ^{f} $\psi = [n(1-R^2)/(n-m)]^{1/2}$; $\psi < 0.02$, very good; $0.02 < \psi < 0.1$, good; $0.1 < \psi < 0.2$, fair; $0.2 < \psi < 0.5$, poor (cf. Exner ref. 18). ^{g} Uncertainties are the 95% confidence intervals. ^{h} (i) Results of correlation using the variables as given in Table S6; (ii) results using standardised variables (cf. ref. 36); (iii) percentage weighting of standardised variables.

Comments on Table S7

Eqn (13) — The correlation of log $[k_2(x)_{SO}/dm^3\ mol^{-1}\ s^{-1}]$ for the oxidation of five cyclic sulfoxides by the change in ring strain between reactants and products. The correlation is 'fair' by Exner's goodness-of-fit criterion but it fails for $(CH_2)_2SO$, underestimating the actual $k_2(3)_{SO}$ by more than two orders of magnitude [see also eqn (S25) below].

Eqn (14) — The correlation of the reactivities of aryl methyl sulfides and sulfoxides together. The values of log $[k_2/dm^3\ mol^{-1}\ s^{-1}]$ used for the aryl methyl sulfides and sulfoxides are not directly experimental values but are read from the least mean squares Hammett plots of experimental relative values, k_X/k_H, and calibrated by direct measurements of k_2 for methyl 4-nitrophenyl sulfide and sulfoxide.[34] The uncertainty in values of the derived absolute second order rate constants is thus minimised within each subset. As is to be expected, therefore, each subset is correlated precisely by $\sigma^*(Ar)$, calculated by the ACD algorithm,[35] since these values are proportional to the Hammett constants σ_m and σ_p, as appropriate. For the aryl methyl sulfides and sulfoxides $\Sigma\sigma^* = \sigma^*(Ar)$, $\sigma^*(Me)$ being zero. Introduction of the additional variable q_S/e results in a single correlation line which is 'good' by Exner's criterion.[18] The strong dependence of the correlation upon q_S/e underlines the importance of the polarity of the sulfoxides (and hence their solvation) in determining their solution reactivity with **1a** relative to that of the sulfides.

Eqn (15) — The correlation resulting from the addition of three extra points for $(n\text{-}Pr)_2S$, $(n\text{-}Pr)_2SO$ and $(t\text{-}Bu)_2SO$ to the data set that gave eqn (14). There is a slight deterioration in precision evidenced by a minor changes in R^2, F and the standard error of the estimate, s, but the value of ψ remains 'good' and the aliphatic data are well correlated with the corresponding less reactive aryl methyl data. As the addition extends the range of $\Sigma\sigma^*$ values from positive to negative also, the weighting of this variable is increased relative to that of q_S/e by comparison with that in eqn (14).

Eqn (16) — The correlation of the reactivities of 24 of the 25 sulfides we have investigated, the exception being $(CH_2)_2S$. This correlation confirms the sensitivity of the reactivity of sulfides generally to the combined steric effects of the carbon ligands on S. It also indicates a similar generality for the frontier orbital term Φ/eV^{-1} which was found to be relevant for the cyclic sulfides in 4.4.

In fact, *all* 25 sulfides are correlated eqn (S24):

$$\log [k_2 /dm^3\ mol^{-1}\ s^{-1}]_{calc} = (2.450 \pm 0.783) + (5.703 \pm 1.875)q_S/e - (1.007 \pm 0.153)\Sigma\sigma^*$$
$$+ (0.337 \pm 0.069)\Sigma E_s' - (7.616 \pm 4.234)\Phi/eV^{-1} \qquad (S24)$$

$R^2 = 0.9821$, $F = 288.6$, $F_{signif} = 2.22 \times 10^{-17}$, $s = 0.093$, $\psi = 0.149$, but we reject this as an artefact since a positive regression coefficient for q_S/e is unreasonable: the rate constant of an electrophilic attack at S will

not increase with increase in the positive charge at S. The inclusion of $(CH_2)_2S$ with its negative Mulliken charge, unique among the sulfides considered (see Table S6), is evidently sufficient to skew eqn (16) into a chemically meaningless form.

Eqn (17) — The correlation of the reactivities of 21 of the 24 sulfoxides we have investigated, the exceptions being $(CH_2)_3SO$, $(CH_2)_4SO$ and $(CH_2)_5SO$. With these exclusions the collinearity of the points for ArSOMe and the dialkyl sulfoxides is conserved and all the remaining points are correlated with somewhat greater precision than were the sulfides by eqn (16). Although the point for $(CH_2)_2SO$ is well accommodated by eqn (17), if it is omitted from the definition of the correlation, all the remaining 23 sulfoxides are correlated by eqn (S25) but this inferior in all respects to eqn (17): R^2 decreases; there is a decrease in F with concomitant increase in F_{signif}; the standard error of the estimate and ψ both increase and the 95% confidence intervals on the intercept and regression coefficients increase irrespective of their direction of change.

$$\log [k_2/dm^3\ mol^{-1}\ s^{-1}] = (1.642 \pm 0.092) - (0.922 \pm 0.084)\Sigma\sigma^*$$
$$- (0.128 \pm 0.053)\Sigma E_s' - (0.033 \pm 0.0078)\Delta E_{rs} \qquad (S25)$$

$R^2 = 0.9784$, $F = 287.6$, $F_{signif} = 5.26 \times 10^{-16}$, $s = 0.079$, $\psi = 0.161$. Furthermore, omission of the point for $(CH_2)_2SO$, does not allow those for $(CH_2)_3SO$, $(CH_2)_4SO$ and $(CH_2)_5SO$ to be correlated with the sulfides (see below).

Eqn (18) — The correlation of the reactivities of all the substrates we have considered with the exception of 5 out of a total of 45. The five exclusions, identified in earlier correlations, are $(t\text{-}Bu)_2S$, $(CH_2)_2S$, $(CH_2)_3SO$, $(CH_2)_4SO$ and $(CH_2)_5SO$. From the value of ψ, the correlation is 'good'. The key ground-state determinants of the reactivity of the correlated compounds are the charge carried at S, the electronic character of the ligands on S and the change in ring-strain, if any, on oxidation. Notable is the absence of a steric factor. If the point for $(t\text{-}Bu)_2S$ is included in defining the correlation, $\Sigma E_s'$ does become significant at a level of probability < 0.01 giving eqn (19) but the precision of correlation deteriorates relative to eqn (18): R^2 decreases; there is a decrease in F with concomitant increase in F_{signif}; the standard error of the estimate increases; the value of ψ declines from 'good' to 'fair' and the 95% confidence intervals on the intercept and regression coefficients increase irrespective of whether the figure itself increases or decreases in magnitude. The reason for this is that whereas the oxidation of sulfides is inhibited by sterically bulky groups, as shown above that of sulfoxides in accelerated. The consequence is that, although the point for $(t\text{-}Bu)_2S$ migrates laterally towards the line, it does not arrive at it as in Fig 5b and, furthermore, the points for $(t\text{-}Bu)_2SO$ and t-butyl 4-nitrophenyl sulfoxide become detached from the line.

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ESI 3 Synthetic Materials

Alkyl 4-nitrophenyl sulfides

The procedure was adapted from that of Courtin and co-workers[1] (see end of section for synthetic references). To a solution of 4-nitro-chlorobenzene (4.73 g, 30 mmol) and the appropriate alkyl thiol (*Stench!*) (60 mmol) in ethanol (30 cm^3) under nitrogen was added, dropwise, a solution of KOH (3.36 g, 30 mmol in 12 cm^3 12% v/v aqueous ethanol); during addition (*ca*. 40 min), the temperature was maintained near 0 °C (ice/water bath) then the mixture was heated under reflux for 2 h. After cooling to ambient temperature, the mixture was diluted with water (50 cm^3) and extracted with dichloromethane (3 × 100 cm^3). The combined extracts were washed with water (2 × 50 cm^3) and dried (Na$_2$SO$_4$). The required products were obtained chromatographically from the crude mixture (column or preparative TLC; elution with 10% v/v Et$_2$O-CH$_2$Cl$_2$ in either case). Yields were sufficient, but indifferent, due to losses on work-up caused by the persistence of unreacted 4-nitro-chlorobenzene.

Ethyl 4-nitrophenyl sulfide

Yellow solid (1.37 g, 25%), mp 42.5–43.5 °C (lit.[2] 43–44 °C); *m/z* 183 (100%, M$^+$), 168 (23), and 109 (22); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 2983 (CH), 1585 and 1355 (NO$_2$); δ_H (270 MHz, CDCl$_3$) 1.38 (t, *J* 7.5, 3H), 3.03 (q, *J* 7.5, 2H), 7.30 (m, 2H) and 8.18 (m, 2H); δ_C (67.9 MHz, CDCl$_3$) 13.6, 26.0, 123.9 (2C), 125.9 (2C), 144.8 and 147.8.

Isopropyl 4-Nitrophenyl sulfide

Yellow solid (0.89 g, 15%), mp 46.3–47.2 °C (lit.[3] 46–47 °C); *m/z* 197 (45%, M$^+$), 155 (78), and 43 (100; v_{max}/cm^{-1}(CH$_2$Cl$_2$) 2968 (CH), 1513(s) and 1340(s) (NO$_2$); δ_H (270 MHz, CDCl$_3$) 1.39 (d, *J* 6.8, 6H), 3.61 (septet, *J* 6.8, 1H), 7.36 (d, *J* 8.0, 2H), 8.12 (d, *J* 8.0, 2H); δ_C (67.9 MHz, CDCl$_3$) 23.4 (2C), 37.2, 123.9 (2C), 127.7 (2C), 144.2 and 147.8.

***n*-Butyl 4-nitrophenyl sulfide**

Yellow oil (2.15 g, 34%), *m/z* 211, (100%, M$^+$), 168 (18) and 109 (18); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 2966 (CH), 1540 and 1344 (NO$_2$); δ_H (270 MHz, CDCl$_3$) 0.96 (t, *J* 7.3, 3H), 1.49 (m, 2H), 1.70 (quintet, *J* 7.3, 2H), 3.02 (t, *J* 7.3, 2H), 7.31 (d, *J* 8.0, 2H), 8.12 (d, *J* 8.0, 2H); δ_C (67.9 MHz, CDCl$_3$) 13.6, 22.0, 30.5, 31.6, 123.9 (2C), 126.0 (2C), 144.8 and 148.1.[4]

***s*-Butyl 4-nitrophenyl sulfide**

Pale yellow oil (1.46 g, 23%), *m/z* 211, (42%, M$^+$), 155 (87) and 57 (100); v_{max}/cm^{-1}(CH$_2$Cl$_2$) 2969 (CH), 1513 and 1340 (NO$_2$); δ_H (270 MHz, CDCl$_3$) 1.05 (t, *J* 7.5, 3H), 1.38 (d, *J* 6.8, 3H), 1.69 (m, 2H), 3.40 (m, 1H), 7.36 (d, *J* 8.5, 2H) and 8.12 (d, *J* 8.5, 2H); δ_C (67.9 MHz, CDCl$_3$) 11.3, 20.2, 29.3, 43.1, 123.8 (2C), 127.6 (2C), 145.9 and 147.3.[5]

t-Butyl 4-nitrophenyl sulfide

Yellow solid (2.9 g, 46%), mp 38.5–39.5 °C (lit.[6] 38–39 °C); *m/z* 211, (5%, M$^+$) and 57 (100); ν_{max}/cm^{-1}(CH$_2$Cl$_2$) 2966 (CH), 1520(s) and 1346(s) (NO$_2$); δ_H (270 MHz, CDCl$_3$) 1.35, (s, 9H), 7.66 (d, *J* 8.8, 2H) and 8.17 (d, *J* 8.8, 2H); δ_C (67.9 MHz, CDCl$_3$) 31.0 (3C), 47.5, 123.3 (2C), 136.8 (2C), 142.3 and 147.7.[7]

Cyclic sulfides

The general method was to react Na$_2$S with the appropriate α,ω-dibromoalkane but the detailed procedure varied from case to case.

Thietane (trimethylene sulfide)

The procedure was adapted from that of Nagasawa and Yoneta.[8] To 1,3-dibromopropane (10 g, 50 mmol) in DMF (250 cm^3), at ambient temperature, was added Na$_2$S [6.5 g, (technical grade, *ca*. 60%), approx. 50 mmol] with continuous stirring over 5 min. The mixture was heated at 135 °C for 20 min and then steam-distilled. The collection of distillate was stopped after 30 min and addition to it of a small quantity of NaCl brought about the separation of organic and aqueous phases. The former was collected and further purified by steam-distillation to yield the required product. Colourless oil (1.33 g, 36%); *m/z* 74 (47%, M$^+$), 46 (100) and 39 (15); ν_{max}/cm^{-1}(CH$_2$Cl$_2$) 2923 (CH); δ_H (270 MHz, CDCl$_3$) 2.89–2.96 (m, 2H) and 3.21 (br. t, *J* 7.0, 4H); δ_C (67.9 MHz, CDCl$_3$) 26.2 (2C) and 28.1.[8,9]

Thiepane (hexamethylene sulfide)

1,6-Dibromohexane (12.1 g, 50 mmol) was stirred with Na$_2$S [7.7 g, (technical grade, *ca*. 60%), approx. 59 mmol] in DMF (250 cm^3) for 16 h at room temperature and the mixture was then steam-distilled. After phase separation, the crude oil was purified by column chromatography (silica, hexane) to give the required product. Colourless oil (0.5 g, 8.6%); *m/z* 116 (88%, M$^+$), 87 (100), 82 (48), 67 (71), 54 (50), and 41 (84); ν_{max}/cm^{-1}(CH$_2$Cl$_2$) 2925(s) and 2847(s) (CH); δ_H (270 MHz, CDCl$_3$) 1.60–1.68 (m, 4H), 1.77–1.88 (m, 4H), and 2.67 (dd, *J* 6.3, 6.1, 4H); δ_C (67.9 MHz, CDCl$_3$) 27.2 (2C), 31.8 (2C) and 34.1 (2C).[9,10]

Thiocane (heptamethylene sulfide)

The method was adapted from those of Singh, Mehotra and Regen[11] and of Mandolini and Vontor.[12] 1,7-Dibromoheptane (2.0 g 7.7 mmol) and sodium sulfide [1.8 g (as Na$_2$S.*x*H$_2$O, where $x \approx 8.2$), approx. 7.7 mmol], each in ethanol (25 cm^3) were added slowly and simultaneously over 6 h, by means of two motorised syringes, to 100 cm^3 refluxing ethanol. After cooling, the mixture was diluted with water (100 cm^3) and extracted with diethyl ether (3 × 100 cm^3). The combined extract was washed with water (100 cm^3) and dried (Na$_2$SO$_4$). The solvent was removed *in vacuo* at 20 °C and the crude product purified by column chromatography (silica, 90% v/v hexane-diethyl ether) to give the required product. Colourless oil (0.12 g, 12%); *m/z* 130 (33%, M$^+$), 129 (100), 85 (30), 69 (45) and 55 (30); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 2925(s) and 2850 (s)

(CH); δ_H (270 MHz, CDCl$_3$) 1.36–1.52 (m, 6H), 1.55–1.67 (m, 4H) and 2.71 (dd, J 5.6, 6.6, 4H); δ_C (67.9 MHz, CDCl$_3$) 25.4, 27.3, 29.4 and 33.3.[9]

Sulfoxides and sulfones

The general method previously described[13] for both types of compound was applied to the sulfides of present concern with appropriate scaling down when necessary.

Methyl 4-nitrophenyl sulfoxide

The preparation was as described previously.[13]

Ethyl 4-nitrophenyl sulfoxide

Yellow solid (89%) mp 76.3–77.8 ºC (lit.[14] 76–78 ºC); m/z 199 (19%, M$^+$), 171 (100), 141 (17), 125 (14) and 77 (14); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3099, 2983 (CH), 1529(s), 1348(s) (NO$_2$), 1055 (SO); δ_H (270 MHz, CDCl$_3$) 1.22 (t, J 8.2, 3H), 2.70–3.07 (m, 2H), 7.34–7.52 (m, 2H) and 7.69–7.74 (m, 2H); δ_C (67.9 MHz, CDCl$_3$) 5.6, 50.1, 124.2 (2C) 125.2 (2C) 149.2 and 151.1.

n-Butyl 4-nitrophenyl sulfoxide

Yellow solid (71%), mp 32.2–34.5 ºC; m/z 227 (7%, M$^+$), 171 (100), 57 (77) and 41 (65); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3099, 2964 (CH), 1529(s), 1348(s) (NO$_2$) and 1043(s) (SO); δ_H (270 MHz, CDCl$_3$) 0.93 (t, J 7.3, 3H), 1.30–1.89 (m, 4H), 2.85 (m, 2H), 7.80 (d, J 8.5, 2H) and 8.38 (d, J 8.5, 2H); δ_C (67.9 MHz, CDCl$_3$) 13.6, 21.8, 23.8, 56.9, 124.3 (2C), 125.1 (2C), 149.8 and 152.2.[15]

s-Butyl 4-nitrophenyl sulfoxide (mixed diastereoisomers)

Waxy yellow solid (65%); m/z 227 (1%, M$^+$), 171 (100), 57 (65) and 41 (39); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 2972 (CH), 1529(s) and 1348(s) (NO$_2$) and 1043 (SO); δ_H (270 MHz, CDCl$_3$) 1.03 (d, J 6.8, 3H), 1.15 (t, J 7.5, 3H), 1.56 (m, 2H), 2.00 (m, 0.5H) and 2.60 (m, 0.5H), 7.4–7.8 (m, 2H) and 8.15–8.47 (m, 2H); δ_C (67.9 MHz, CDCl$_3$) 10.1, 11.1, 24.3, 61.6, 124.0 (2C), 125.7 (2C) 142.5 and 150.2.[16]

t-Butyl 4-nitrophenyl sulfoxide

Yellow solid (87%), mp 100.6–101.9 ºC (lit.[17] 101–102 ºC); m/z (227<1%, M$^+$), 171 (8), 57 (100) and 41 (23); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 2966 CH), 1529(s) and 1349(s) (NO$_2$) and 1047 (SO); δ_H (270 MHz, CDCl$_3$) 1.21 (s, 9H), 7.79 (d, J 8.5, 2H) and 8.36 (d, J 8.5, 2H); δ_C (67.9 MHz, CDCl$_3$) 22.7 (3C), 57.0, 123.4 (2C), 127.3 (2C), 147.9 and 149.6.

Di-(*n*-propyl) sulfoxide

Colourless oil (80%); *m/z* 134 (5%, M$^+$), 43 (96), 41 (100) and 39 (73); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 3049, 2969 (CH) and 1018(s) (SO); δ_H (270 MHz, CDCl$_3$) 1.02 (t, *J* 7.3, 6H), 1.68–1.80 (appt. sextet, 4H), and 2.46–2.67 (m, 4H); δ_C (67.9 MHz, CDCl$_3$) 13.3, 16.1 and 54.2.[18]

Di-(*n*-propyl) sulfone

Colourless solid (73%), mp 29.8–30.6 °C (lit.[19] 29.5–30 °C); *m/z* 150 (0.4%, M$^+$) and 43 (100); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 3060, 2973 (CH), 1311(s) and 1132(s) (SO$_2$); δ_H (270 MHz, CDCl$_3$) 1.02 (t, *J* 7.6, 6H), 1.73–1.85 (m, 4H) and 2.80–3.00 (m, 4H); δ_C (67.9 MHz, CDCl$_3$) 12.9, 15.5 and 54.1.[20]

Di-(t-butyl) sulfoxide

Colourless solid (79%), mp 63.1–63.6 °C (lit.[21] 62–63 °C); *m/z* 162 (0.7%, M$^+$) and 57 (100); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 2966 (CH) 1471 and 1367 (CH$_3$) and 1029 (SO); δ_H (270 MHz, CDCl$_3$) 1.33 (s); δ_C (67.9 MHz, CDCl$_3$) 25.5 (6C) and 57.1 (2C).[22]

Di-(*t*-butyl) sulfone

Colourless solid (76%), mp 129.5–130.5 °C (lit.[23] 128–129 °C); *m/z* 196 (100%, M+NH$_4$$^+$), 140 (30), 123 (15), 57 (12); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 3054, 2977 (CH); 1475, 1371 (CH$_3$), 1274(s) and 1097(s) (SO$_2$); δ_H (270 MHz, CDCl$_3$) 1.44 (s); δ_C (67.9 MHz, CDCl$_3$) 26.0 and 64.7.[24]

Thiirane 1-oxide (ethylene sulfoxide)

Colourless oil (65%); *m/z* 76 (48%, M$^+$) and 27 (100); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 3050, 2983 (CH) and 1088(s) (SO); δ_H (270 MHz, CDCl$_3$) 2.01–2.08 (m, 2H) and 2.47–2.54 (m, 2H); δ_C (67.9 MHz, CDCl$_3$) 34.2 (2C).[9]

Thietane 1-oxide (trimethylene sulfoxide)

Colourless oil (78%); *m/z* 90 (51%, M$^+$) and 41 (100); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 3052, 2981 (CH) and 1097(s) (SO); δ_H (270 MHz, CDCl$_3$) 1.98–2.06 (m, 1H), 2.20–2.37 (m, 1H), 3.11–3.26 (m, 2H) and 3.43–3.52 (m, 2H); δ_C (67.9 MHz, CDCl$_3$) 10.7 and 53.1 (2C).[9]

Thietane 1,1-dioxide (trimethylene sulfone)

Colourless solid (65%), mp 74.5–75.6 °C (lit.[25] 73–75 °C); *m/z* 106 (<1%, M$^+$), 78 (5), 64 (4), 42 (100) and 41 (76); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 3056 (CH), 1322(s) and 1133(s) (SO$_2$); δ_H (270 MHz, CDCl$_3$) 2.1 (m, 2H) and 4.12 (t, *J* 8.4, 4H); δ_C (67.9 MHz, CDCl$_3$) 5.7 and 65.5 (2C).[9]

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Thiolane 1-oxide (tetramethylene sulfoxide or tetrahydrothiophen 1-oxide)

Colourless oil (83%); m/z 104 (50%, M$^+$), 63 (32) and 55 (100); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3051, 2971 (CH) and 1020(s) (SO); δ_H (270 MHz, CDCl$_3$) 1.80–2.20 (m, 2H), 2.30–2.50 (m, 2H) and 2.70–2.82 (m, 4H); δ_C (67.9 MHz, CDCl$_3$) 25.7 (2C) and 54.7 (2C).[9]

Thiolane 1,1-dioxide (tetramethylene sulfone or tetrahydrothiophen 1,1-dioxide)

Colourless solid (76%), mp 27.9–28.7 °C (lit.[60] 28.6 °C); m/z 120 (20%. M$^+$), 56 (64), 55 (51) and 41 (100); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3062, 2950 (CH), 1274(s) and 1126(s) (SO$_2$); δ_H (270 MHz, CDCl$_3$) 2.15–2.20 (m, 4H), 2.95–3.01 (m, 4H); δ_C (67.9 MHz, CDCl$_3$) 23.0 (2C) and 51.4 (2C).[9, 26]

Thiane 1-oxide (pentamethylene sulfoxide or tetrahydrothiopyran 1-oxide)

Colourless solid (72%), mp 60.4–61.7 °C (lit.[27] 60–61.5 °C); m/z 118 (40%, M$^+$), 69 (61), 63 (55) and 41 (100); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3051, 2942 (CH) and 1031(s) (SO); δ_H (270 MHz, CDCl$_3$) 1.45–1.62, (m, 4H) 2.10–2.20 (m, 2H) and 2.60–2.84 (m, 4H); δ_C (67.9 MHz, CDCl$_3$) 19.2, 24.8 (2C) and 49.1 (2C).[9, 28]

Thiane 1,1-dioxide (pentamethylene sulfone or tetrahydrothiopyran 1-oxide)

Colourless solid (61%), mp 101.1–102.5 °C (lit.[29] 100.5–102 °C); m/z 134 (15%, M$^+$), 69 (47), 55 (33), 42 (100) and 41 (64); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3060, 2951 (CH), 1299(s) and 1106(s) (SO$_2$); δ_H (270 MHz, CDCl$_3$) 1.55–1.63 (m, 2H), 2.04 (m, 4H) and 2.95 (t, J 6.3, 4H); δ_C (67.9 MHz, CDCl$_3$) 24.1, 24.5 (2C) and 52.4 (2C).[9, 28, 30]

Thiepane 1-oxide (hexamethylene sulfoxide)

Colourless solid (62%), mp 62.1–62.9 °C;[31] m/z 132 (9, M$^+$), 115 (100), 55 (66) and 41 (76); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3051, 2935 (CH) and 1028(s) (SO); δ_H (270 MHz, CDCl$_3$) 1.50–1.80 (m, 6H), 2.00–2.30 (m, 2H), and 2.80–3.0 (m, 4H); δ_C (67.9 MHz, CDCl$_3$) 19.2 (2C), 26.8 (2C) and 52.4 (2C).[9]

Thiepane 1,1-dioxide (hexamethylene sulfone)

Colourless solid (69%), mp 71.2-71.9 °C (lit.[32] 71-71.5 °C); m/z 148 (8%, M$^+$), 54 (85), 55 (100) and 41 (90); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3057, 2937 (CH), 1288(s) and 1118(s) (SO$_2$); δ_H (270 MHz, CDCl$_3$) 1.73–1.82 (m, 4H), 1.91–2.00 (m, 4H) and 3.10–3.20 (m, 4H); δ_C (67.9 MHz, CDCl$_3$) 21.7, 27.4 and 56.1.[9]

Thiocane 1-oxide (heptamethylene sulfoxide)

Colourless solid (58%), mp 60.8–61.7 °C (lit.[33] 61–62 °C); m/z 164 (2% M + NH$_4^+$), 147 (100%, M + H$^+$) and 129 (15); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3053, 2929 (CH) and 1024(s) (SO); δ_H (270 MHz, CDCl$_3$) 1.20–2.20 (m, 10H) and 2.94–3.10 (m, 4H); δ_C (67.9 MHz, CDCl$_3$) 21.3 (2C), 25.2, 26.2 (2C) and 52.9 (2C).[9]

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Thiocane 1,1-dioxide (heptamethylene sulfone)

Colourless solid (85%), mp 74.3–75.6 °C (lit.[33] 74–75 °C); m/z 162 (1%, M$^+$) 145 (3) 70 (30), 69 (30) and 55 (100); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 2929 (CH), 1292(s) and 1118(m) (SO$_2$); δ_H (270 MHz, CDCl$_3$) 1.65–1.77 (m, 6H), 2.00–2.13 (m, 4H) and 3.15– 3.20 (m, 4H); δ_C (67.9 MHz, CDCl$_3$) 22.4 (2C), 23.8, 26.7 (2C) and 54.1 (2C).[9]

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ESI 4 Table S8 Rate constants for the oxidation of cyclic sulfides by NaIO$_4$ in 50% v/v aqueous ethanol at 298 K

Substrate	Ring size, x	$10^2 k_2(x)$/dm^3 mol^{-1} s^{-1} [a]	$[k(x)/k(n\text{-Pr})_2]_{\text{sulfide}}$ [b]
Thiirane	3	17.0 ± 1.0 [c]	0.72 [d]
Thietane	4	24.3	1.02
Thiolane	5	71.4	3.01
Thiane	6	39.9	1.68
Thiepane	7	33.7	1.40
$(n\text{-Pr})_2$S		23.7	1.00

[a] Data from F. Ruff and A. Kucsman, *J. Chem. Soc., Perkin Trans. 2*, 1985, 683 except for entry 1. [b] Data for plot 3 of Fig. 2 (main paper). [c] Calculated as $[k(3)/k(6)]_{\text{sulfide}} \times 0.399$. [d] Calculated as $[k(3)/k(6)]_{\text{sulfide}} \times 0.399/0.237$, see Experimental (main paper).