and to stabilize the latter.[3,52] In view of the above discussion these functions may be interpreted as different aspects of the same cause, namely a structural and electronic perturbation of the substrate by the enzyme everywhere along the reaction profile. In the ground state small but specific structural and electronic changes in the bonded substrate are induced, the associated cost in enthalpy and entropy being modest and/or overcompensated by binding energy. The perturbation changes dramatically on going to the transition state. Resulting rates of change may amount to as much as 10 kcal in free energy of activation per 0.05 Å of ground-state structural change (Figure 3), corresponding to an acceleration of 10^7 at room temperature. The structural changes necessary for significant changes in rate may be compared, for example, with the observed variation of C=O and C-N equilibrium distances in amides. They depend on the degree of protonation and vary from 1.24 and 1.35 Å for a standard amide group in a helix or pleated sheet structure to 1.28 and 1.30 Å, respectively, in a hemiprotonated amide group (RHN-RCO···H···OCR-NHR).[52] Thus, even partial protonation induces structural changes large enough to account for significant changes in reactivity.

For many reactions, especially organic ones, the differences in ground-state structures may be quite small, whereas the associated rate differences may be relatively large. This points to a need for accurate structure determinations for a series of molecules, preferably in conjunction with corresponding kinetic and mechanistic experiments. Significant structural differences indicating incipient reaction toward the transition state and corresponding kinetic differences are likely to be found whenever a steric or electronic difference between related reactants can be identified. In these cases ground-state structure is related to reactivity in a quantitative and predictable way.

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Supplementary Material Available: Tables of scaled internal coordinates and inertial coordinates and a figure with results of principal component analysis (5 pages). Ordering information is given on any current masthead page.

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S–S Bond Lengths, or Can a Bond Length Be Estimated from a Single Parameter?

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Abstract: The results of 6-31G* optimizations of the equilibrium molecular geometries of S_2^ϵ ($-2 \le \epsilon \le +2$), $X(SS)_2^\epsilon$ (C_2; X = P, S, Cl; $-3 \le \epsilon \le -1$), $SO_{4-n}S_n^{2-}$ (n = 1–4), S_2O, X_2S_2 (C_2; X = H, F, Cl), and SSF_2 are reported in detail and compared with experiment. The calculated bond lengths r_e(S–S) in these molecular species exhibit a high degree of correlation (r^2 = 0.97) with the electron densities $\rho(r_c)$ at the critical points in these bonds, $r_e(\text{S–S}) = 1.229[\rho(r_c)]^{-0.269}$. This power-law relationship, the analogue of which has been demonstrated for Al–F, O–O, and Be–Cl bonds and which is expected to be of general validity, makes possible estimates of r_e from $\rho(r_c)$ and, conversely, estimates of $\rho(r_c)$, bond order, and related properties from r_e.

The answer to the title question appears to be a cautious yes. The parameter is the electron density $\rho(r_c)$ at the bond critical point, i.e., at the point where the density is a minimum with respect to a displacement along the bond path but a maximum with respect to a lateral displacement ($\nabla\rho(r_c) = 0$).[1,2] In the following we demonstrate the existence of a simple correlation between the bond length r_e and $\rho(r_c)$ for S–S bonds, both obtained from 6-31G* optimizations[3-5] of the equilibrium geometries of a number of simple molecular species. While the present demonstration involves *calculated* r_e (Å) and $\rho(r_c)$ (au), we have no reason to suppose that it would not apply equally to experimental $r_e,\rho(r_c)$ pairs. Since $\rho(r_c)$ is accessible to experiment with difficulty, the practical value of the correlation may well be in its reverse, i.e., using the bond length to estimate $\rho(r_c)$ and in turn quantities related to it, e.g., the bond order[2] or, in a more restrictive context, the force constants of S–S bonds.[6] However, the main point we wish to make is that the existence of such a correlation within a given optimization scheme is by itself of interest, regardless of the merits or demerits of our particular 6-31G* basis set in relation to experiment or to other theoretical treatments.

Table I. Optimized Equilibrium Molecular Parameters (6-31G*) of S_2^ϵ Species

				S–S, Å	
No.	species	$E_{6\text{-}31G^*}$, au	$\rho(\mathbf{r}_c)$, au	calcd	obsd
1	S_2 ($X^3\Sigma_g^-$)	−795.016 58	0.205 47	1.8782	1.8894[8]
2	S_2 ($a^1\Delta_g$)	−794.964 06	0.205 59	1.8779	1.8983[9]
3	S_2^+ ($X^2\Pi_g$)	−794.669 06	0.243 79	1.7879	1.8240 (2)[10]
4	S_2^{2+}	−794.046 21	0.275 79	1.7196	
5	S_2^-	−795.046 26	0.160 46	2.0000	
6	S_2^{2-}	−794.847 48	0.104 81	2.2020	*a*

[a] The values observed in crystals range from ~2.03 to ~2.36 Å. They depend strongly on the nature of the countercation and on the physical properties of the crystal. The two values included in the inset of Figure 1 are those for the two much studied forms of FeS_2, pyrite, and marcasite (unlabeled).

The r_e vs. $\rho(r_c)$ correlation for S–S bonds is based on an extension of our 6-31G* treatment of isoelectronic XL_4^ϵ species.[7]

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Table II. Optimized (6-31G*) Equilibrium S–S Bond Lengths (Å) and Electron Densities $\rho(\mathrm{r_c})$ (au) at the Critical Points in the S–S Bonds, Together with Literature Values of S–S Bond Lengths

no.	species	$\rho(\mathbf{r}_c)$	bond length calcd	bond length obsd[a]
7	$P(S'S'')_2^{3-}$, C_2	0.116 85	2.1587	
	$S(S'S'')_2^{2-}$, C_2:			K_2S_5 xd[11]
8	S – S′	0.141 85	2.0815	⟨2.075(6)⟩
9	S′ – S″	0.133 55	2.0903	⟨2.044(12)⟩
10	SS'^{2-}_4, T_d	0.145 53	2.0548	
11	SOS'^{2-}_3, C_{3v}	0.156 01	2.0417	
12	$SO_2S'^{2-}_2$, C_{2v}	0.159 02	2.0479	
13	$SO_3S'^{2-}$, C_{3v}	0.157 98	2.0644	$MgS_2O_3 \cdot 6H_2O$ xd,[12] 2.013 (3) $Na_2S_2O_3 \cdot 5H_2O$ nd,[13] 2.024 (4)
14	$Cl(S'S'')_2^-$, C_2	0.190 76	1.9135	
15	S′SO, C_s	0.215 84	1.8674	mw,[14] 1.8852 (22)
16	HSSH, C_2	0.148 09	2.0633	ed,[15] 2.05 (2); 3-21G*,[16] 2.0573
17	FSSF, C_2	0.190 03	1.9534	mw,[17] 1.888 (10)
18	$S'SF_2$, C_s	0.196 58	1.8793	mw,[17,18] 1.860 (15)
19	ClSSCl, C_2	0.168 59	2.0040	ed,[19] 1.97 (3); mw,[20] 1.9504 (12)

[a] xd, X-ray diffraction; nd, neutron diffraction; ed, electron diffraction; mw, microwave spectroscopy; 3-21G*, ab initio calculation.

The results of this extension (Tables I–III) are all new. Where comparison with experiment can be made, the calculated bond lengths are seen (Tables I and II, inset of Figure 1) to agree, on the average, with the experimental values to within ~0.03 Å (for a more general comparison see ref 7) except where special circumstances exist (see below). The present account is confined mainly to a discussion of the bond lengths; we reserve comments on other aspects of these results for a later occasion.

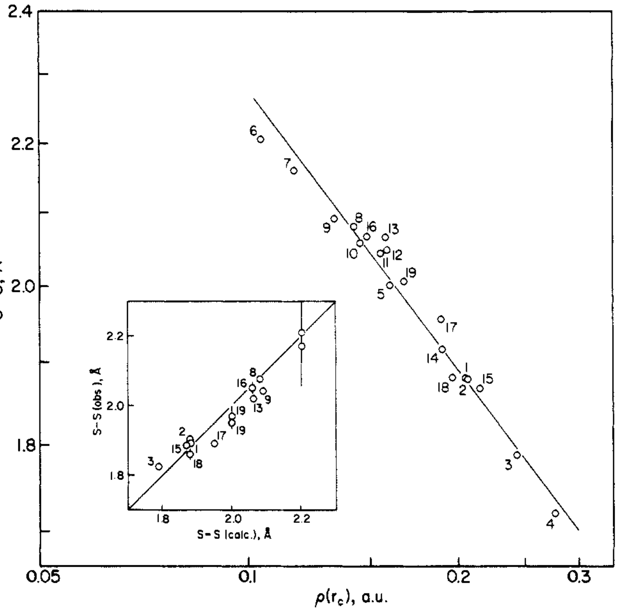

Figure 1. A log $(S–S)_{6\text{-}31G^*}$ vs. log $\rho(\mathbf{r}_c)_{6\text{-}31G^*}$ plot for sulfur species **1**–**19** (Tables I and II). Inset: comparison of 6-31G* and observed values of the S–S bond lengths. For the two unlabeled points, see Table I.

Since $\rho(\mathrm{r_c})$ is *a* measure of the bond strength, it is reasonable to expect a decrease in $\rho(\mathrm{r_c})$ with an increase in r_e. The simplest functional relationship consistent with $r_e \rightarrow \infty$ as $\rho(\mathrm{r_c}) \rightarrow 0$ is a power law. The bond length r_e(S–S), which results directly from

Table III. Total Electronic Energies $E_{6\text{-}31G^*}$ (au), Bond Lengths (Å), Bond Angles (deg), Critical Radii r_c (Å), Net Charges ϵ(S) and ϵ(L), Electron Densities at the Bond Critical Points $\rho(\mathrm{r_c})$ (au), and Dipole Moments (D) for Optimized Geometries of Molecular Species of Table II

no.	species	$E_{6\text{-}31G^*}$	S–L	bond angle	r_c	ϵ(S), ϵ(L)	$\rho(\mathbf{r}_c)$	μ
7	$P(S'S'')_2^{3-}$	−1930.471 31	P – S′, 2.1790	S′PS′, 112.03 PS′S″, 117.10 S′PS′/PS′S″, 85.65	P, 0.8993 $S'_{PS'}$, 1.2797 $S'_{S'S''}$, 1.1045	S′, −0.398 S″, −0.924 P, −0.357	P – S′, 0.108 62	1.172
8, 9	$S(S'S'')_2^{2-}$	−1987.517 00	S – S′, 2.0815	S′SS′, 111.52[a] SS′S″, 110.70[a] S′SS′/SS′S″, 84.13[a]	S, 1.0596 $S'_{SS'}$, 1.0219 $S'_{S'S''}$, 1.1148	S′, −0.178 S″, −0.742 S, −0.160	S – S′, 0.141 85	1.959
10	SS'^{2-}_4	−1987.465 60	S – S′, 2.0548	S′SS′, 109.47	S, 1.1521	S′, −0.585 S, 0.340	S – S′, 0.145 53	0
11	SOS'^{2-}_3	−1664.792 95	S – O, 1.4736	S′SO, 109.74 S′SS′, 109.21	$S_{SS'}$, 1.1328 S_{SO}, 0.5670	S′, −0.687 O, −0.770 S, 0.831	S – O, 0.279 93	0.030
12	$SO_2S'^{2-}_2$	−1342.129 04	S – O, 1.4676	S′SO, 108.73 S′SS′, 109.46 OSO, 112.41	$S_{SS'}$, 1.1201 S_{SO}, 0.5638	S′, −0.796 O, −0.788 S, 1.167	S – O, 0.283 33	0.564
13	$SO_3S'^{2-}$	−1019.462 11	S – O, 1.4724[b]	S′SO, 108.08[b] OSO, 110.83[b]	$S_{SS'}$, 1.1099 S_{SO}, 0.5642	S′, −0.915 O, −0.823 S, 1.383	S – O, 0.282 09	
14	$Cl(S'S'')_2^-$	−2049.500 29	Cl – S′, 2.6214	S′ClS′, 117.79 ClS′S″, 113.22 S′ClS′/ClS′S″, 71.21	Cl, 1.3867 $S'_{ClS'}$, 1.2347 $S'_{S'S''}$, 1.0093	S′, 0.084 S″, −0.312 Cl, −0.545	Cl – S′, 0.038 92	1.686
15	S′SO	−869.806 79	S – O, 1.4357[c]	S′SO, 117.36[c]	$S_{SS'}$, 1.1222 S_{SO}, 0.5565	S, 0.771 S′, −0.281 O, −0.553	S – O, 0.288 54	1.908
16	HSSH	−796.174 39	S – H, 1.3271[d]	SSH, 99.11[d] HSS/SSH, 90.01[d]	S_{SS}, 1.0316 S_{SH}, 0.8515	S, −0.116 H, 0.116	S – H, 0.217 43	1.560
17	FSSF	−993.824 04	S – F, 1.6109[e]	SSF, 104.26[e] FSS/SSF, 88.65[e]	S_{SS}, 0.9770 S_{SF}, 0.6284	S, 0.435 F, −0.435	S – F, 0.175 22	1.702
18	$S'SF_2$	−993.813 95	S – F, 1.5787[f]	S′SF, 107.90[f] FSF, 92.12[f]	S_{SS}, 1.2211 S_{SF}, 0.6161	S′, −0.327 F, −0.395 S, 1.117	S – F, 0.193 27	1.877
19	ClSSCl	−1713.949 66	S – Cl, 2.0404[g]	SSCl, 105.86[g] ClSS/SSCl, 85.10[g]	S_{SS}, 1.0024 S_{SCl}, 0.9494	S, 0.156 Cl, −0.156	S – Cl, 0.144 73	1.074

[a] Reference 11: S′SS′, 106.4 (1)°; SS′S″, ⟨109.2 (6)°⟩; S′SS′/SS′S″, ⟨71.2 (25)°⟩. [b] Reference 12: S – O, 1.467 (8) Å; S′SO, ⟨108.7 (10)°⟩; OSO, ⟨110.2 (10)°⟩. Reference 13: S – O, ⟨1.467 (13)⟩ Å; S′SO, ⟨108.1 (10)°⟩; OSO, ⟨110.8(10)°⟩. [c] Reference 14: S – O, 1.4586(19) Å; S′SO, 117.91°. [d] Reference 15: S – H, 1.33 Å; SSH, 95°; HSS/SSH, 90° (all assumed). Reference 16: 3-21G*: S – H, 1.3273 Å; SSH, 99.00°; HSS/SSH, 89.78°; $E = -792.483\,18$ au. [e] Reference 17: S – F, 1.635 (10) Å; SSF, 108.3(5)°; FSS/SSF, 87.9(15); μ, 1.45(2) D. [f] References 17 and 18: S – F, 1.598 (12) Å; S′SF, 107.5 (10)°; FSF, 92.5 (10)°; μ, 1.03(3) D. [g] Reference 19: S – Cl, 2.07 (1) Å; SSCl, 107 (2.5)°; ClSS/SSCl, 82.5 (12)°. Reference 20: S – Cl, 2.0552 (7) Å; SSCl, 107.66 (5)°; ClSS/SSCl, 85.24 (10)°.

Table IV. Comparison of Linear and Power Regressions of $\rho(\mathbf{r}_c)$ on r_e (Calculated[a] Values)

	linear fit		power fit	
bonds	r^2	σ, au	r^2	σ, au
C–C ($n = 4^b$),[2] STO-3G	0.995	0.005	0.972	0.012
C–C ($n = 4^b$),[2] 6-31G	0.999	0.002	0.984	0.014
C–C ($n = 32$),[2] STO-3G	0.960	0.009	0.949	0.010
C–N ($n = 20$)[23]	0.987	0.009	0.972	0.011
S–S ($n = 6$, S_2^e only)[c]	0.986	0.008	0.995	0.006
S–S ($n = 19$)[c]	0.977	0.007	0.968	0.007
O–O ($n = 6$, O_2^e only)[d]	0.943	0.065	0.971	0.059
O–O ($n = 16$)[d]	0.950	0.050	0.983	0.029
Al–F($n = 35$)[d]	0.959	0.005	0.994	0.002
Be–Cl ($n = 7$)[d]	0.955	0.008	0.996	0.003

[a] 6-31G* optimization unless stated otherwise; n = number of $r_e, \rho(\mathbf{r}_c)$ pairs. [b] C_2H_6, C_2H_4, C_2H_2, and C_6H_6 only. [c] This work. [d] Details to be published.

the optimization process, was deemed the more reliable of the two parameters; hence the 19 $\rho(r_c)$ values of Tables I and II were regressed on r_e. The coefficient of determination r^2 of the regression was 0.968. The regression equation was then converted to $r_e(\text{S–S}) = 1.2291[\rho(r_c)]^{-0.2687}$, $\sigma = 0.026$ Å. Considering the variety of the sulfur species included in the sample and the width of the r_e range, ~1.7 to ~2.2 Å, this goodness of fit is regarded as evidence that a power-law correlation between the calculated r_e and $\rho(r_c)$ indeed exists.[21]

The existence of corresponding $r_e,\rho(r_c)$ correlations has also been demonstrated for several other types of bonds (Table IV). This would suggest that the relationship may hold for *any* class of (binary) bonds; i.e., r_e depends on the *resultant* electron density at the critical point, regardless of the origin and magnitude of the individual contributions to $\rho(r_c)$ from particular MOs (a point already made for C–C bonds in hydrocarbons[2]). When a bond is very long, special reasons may exist which render the SCF procedure inadequate for reproducing the observed r_e, but the *experimental* $r_e,\rho(r_c)$ pairs would be expected to follow the correlation even for such extreme cases of bonding.[22] We are at present engaged in examining the applicability of the correlation to other classes of bonds in molecular species optimized at the 6-31G* level.

The problem of correlating r_e and $\rho(r_c)$ is, however, not entirely without ambiguity. Two such correlations were reported previously, one for C–C bonds in a variety of hydrocarbons,[2] the other for C–N bonds in 23 small molecules.[25] In both cases $\rho(r_c)$ was regressed on r_e *linearly*; the goodness of fit was in no way suggestive of a necessity to investigate alternative modes of regression. Although a linear function does not satisfy the asymptotic requirements and cannot therefore describe the relationship of r_e and $\rho(r_c)$ correctly, it is conceivable that it could approximate the power law over a limited range of r_e with reasonable statistical fidelity. To test this possibility we refitted the data of refs 2 and 25. Surprisingly, the linear fit was in both cases somewhat better than the power fit. Comparison of the linear and power regressions of $\rho(r_c)$ on r_e for *all* the currently available $r_e,\rho(r_c)$ data sets shows that of the 10 sets and subsets of Table IV, those for Al–F, Be–Cl, O–O, and S–S in S_2^e are better fitted to a power function, whereas the others give a better fit to a linear function or are indifferent. Evaluation of these results is complicated by the inequality of the basis sets and of sample sizes. However, closer scrutiny seems to suggest that the discrepancy between the expectation from the model function with the correct characteristics (the power law) and the regression actually obtained is due to sampling problems, and that better designed and more complete sample sets can be expected to vindicate the essential validity of the power-law correlation. This matter is being investigated further.

Tables II and III afford an opportunity to compare the $E_{6\text{-}31G^*}$ values for two pairs of isomers. The SS_4^{2-} (C_2) (**8**, **9**) isomer is about 0.05 au ~ 32 kcal/mol lower in energy than SS_4^{2-} (T_d) (**10**); this agrees with observation to the extent that only the C_2 isomer appears to have been reported.[11] The other pair of topological isomers, FSSF (**17**) and SSF_2 (**18**), differs in E by only 0.01 au ~ 6 kcal/mol in favor of FSSF, whereas at ordinary temperatures SSF_2 is the more stable form.[26,27] However, the difference in E is too small in relation to the uncertainty of SCF-optimized energies of species involving fluorine[7] for it to be of any predictive value.

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(21) The estimated limiting discrepancy of ~0.03 Å between 6-31G* and experimental bond length values would translate into an uncertainty in $\rho(r_c)$ of about 0.006 au (~3% of the $\rho(r_c)$ range of Figure 1) at the upper end of the S–S range, and about 0.02 au (~10% of the $\rho(r_c)$ range) at the lower end of the S–S range.

(22) In the dithionite ion, *cis*-$(O_2SSO_2)^{2-}$, the S–S bond length is 2.39 Å,[23,24] and its inclusion would significantly extend the r_e, $\rho(\mathbf{r}_c)$ range of Figure 1. However, the 6-31G* optimized bond length falls 0.15 Å short of the observed value, indicating the inadequacy of the 6-31G* basis set (and indeed any HF basis set, cf. ref 24) to deal with such abnormal situations.

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