DOI: 10.1002/ejic.200800880

The Variable Strength of the Sulfur–Sulfur Bond: 78 to 41 kcal – G3, CBS-Q, and DFT Bond Energies of Sulfur (S_8) and Disulfanes XSSX (X = H, F, Cl, CH_3, CN, NH_2, OH, SH)

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Keywords: Sulfur / Radicals / Density functional calculations / Thermochemistry / Bond order / Spin density

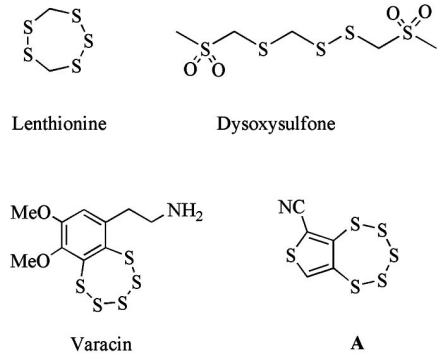
Experimental values for the strength of the sulfur–sulfur bond scatter over a wide range and are frequently in disagreement with each other. For S_8, reliable experimental data seem to lack entirely. To check experimental data and establish the strength of the sulfur–sulfur bond in S_8, high-precision thermochemical calculations (G3, CBS-Q) and DFT methods were employed. The calculations confirm a stunning range for the strength of the sulfur–sulfur bond with energies between 77.7 kcal for FSSF and only 41.8 kcal for tetrasulfane, HSS–SSH. For the pivotal bond energy of elemental sulfur, S_8, the bond energy is 40.5 kcal but can be narrowed to 38.0–39.2 kcal mol^{-1} by including CBS-QB3 data. While older DFT methods are not well suited to accurately reproduce the S–S bond energies, excellent data can be obtained with the recently introduced Boese–Martin (BMK) hybrid DFT method. Atoms in molecules (AIM) calculations reveal significant multiple bonding and spin delocalization in the sulfur radicals XS$^{\cdot}$.

Introduction

The sulfur–sulfur bond[1] is an omnipresent structural motif. The extensive crosslinking of polyisoprene, a linear polymer of poor chemical stability, with disulfane and trisulfane bridges is the chemical basis for the manufacturing of vulcanized rubber, the first industrially produced elastomer.[2,3] Dichlorodisulfane, S_2Cl_2, the solvent used in the process, is an important industrial intermediate in its own right.[4]

At elevated temperatures, sulfur–sulfur bonds dissociate rather easily, as the polymerization of S_8 into, inter alia, *catena*-sulfur slightly above its melting point (158 °C) illustrates.[5] The facile cleavage of sulfur–sulfur bonds can have rather unexpected consequences: The presence of polysulfanes HS(S)$_n$SH in sour natural gases is now recognized as a calamity, because their disproportionation can lead to sulfur deposits blocking gas pipelines.[6]

A wide range of naturally occurring disulfanes, tetrasulfanes, and pentasulfanes with potent antibiotic, antifungal, and even antineoplastic activity like lenthionine,[7,8] varacin,[9] and dysoxysulfone[10] have been isolated from plants and fungi. The in vitro antitumor activity of extracts from such common cultivated plants like leeks, garlic, and onions has likewise been ascribed to the presence of organic disulfides and polysulfides.[1a,11,12d] Synthetic benzopentathiepines like **A** were studied by Chenard's group at Dupont and now represent an important class of antifungal agents (Scheme 1).[13]



Scheme 1.

In view of the multifaceted importance of natural and synthetic disulfanes and polysulfanes, it is surprising that the strength of the sulfur–sulfur bond is not well established.[14]

Textbooks[15] and reference manuals[16] typically give a "generic" value of either 54 or 64 kcal mol^{-1}. While the two values deviate from each other, one might at least assume that they represent average values resulting from a large number of data points. A closer look at the underlying experimental data reveals quite the opposite. Experimental data are scarce, characterized by large or even unspecified error margins, or are in conflict with each other. Accurate

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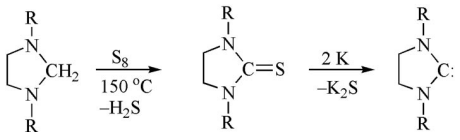
data on the pivotal bond energy of sulfur (S_8) seem to be lacking entirely. Even a cursory inspection of the published data shows that the range for the strength of the sulfur bond must be much wider than the generic values of 54 and 64 kcal would suggest. For disulfane, HSSH, the reported value is 66.0 ± 2 kcal.[17] For the closely related dimethyldisulfane, two conflicting values of 65.3 ± 1 kcal[18a] and 72.4 ± 1.5 kcal[18b] are available. For elemental sulfur, S_8, the situation is rather obscure. A bond energy of 32.8 kcal mol^{-1} is favored in the comprehensive critical review on the thermochemistry of sulfur compounds by Benson,[17] but the error margin of this value is not clear and the underlying experimental sources give a value of "about 35 kcal" without giving further details.[20] A value of 27.5 ± 5 kcal was obtained by Powell and Eyring in 1943 in their comprehensive analysis of the molten sulfur system, but this value refers to the formation of *catena*-sulfur from S_8, not to the ring opening of S_8 per se.[19] The only other experimental value for extended chains of sulfur atoms seems to be that for dimethyltetrasulfane: a value of ca. 35 kcal was determined for the central bond by Kende et al.[20] A reinvestigation by Hawari and Griller gave a value of 32.3 ± 1 kcal mol^{-1}, reasonably close to Kende's value.[21] The low bond energy of dimethyltetrasulfane points to a similarly low bond energy in S_8, but this is of course circumstantial evidence at best. For difluorodisulfane, FSSF, we are confronted with no less than three conflicting literature values. While Benson's review gives a value of 61.0 ± 4.0 kcal, a bond energy of 77 kcal is given by Lösking et al.[57] The current (August 2008) US National Institute of Standards (NIST) web database gives enthalpies of formation for the SF$^{\cdot}$ radical and S_2F_2 that translate into yet another bond dissociation energy: 86.6 kcal.[58]

The highest bond energy for a sulfur–sulfur bond (99.2 kcal mol^{-1}) has been obtained for the reactive intermediate S_2 by Huber and Herzberg in one of their groundbreaking spectroscopic studies.[22,23] Even if S_2 is excluded, literature values for the sulfur–sulfur single bond in disulfanes, polysulfanes, and S_8 still cover the astonishing range of 32.8 kcal mol^{-1} to 86.6 kcal mol^{-1}.

Our interest in the precise strength of the sulfur–sulfur bond was triggered by synthetic and mechanistic questions arising from the C–H activation of formaldehyde aminals with S_8, a reaction that allows the synthesis of sterically hindered thioureas,[24] which we have used as starting materials for the synthesis of stable Wanzlick carbenes[25] (Scheme 2).



Scheme 2.

Replacing elemental sulfur with potentially more reactive disulfanes or polysulfanes is of interest to generalize this approach. As the scarcity and the contradictions in experimental sulfur–sulfur bond energies give little thermodynamic guidance, we have investigated the issue by obtaining high-precision CBS-Q and G3 bond energies for a series of representative disulfanes XSSX (X: H, F, Cl Me, CN, HO, H_2N, and H), tetrasulfane, HSSSSH, and sulfur, S_8. As the significant computational demands of high-precision thermochemical calculations render them impractical for systems with more than 8–10 heavy atoms, the suitability of advanced DFT methods was investigated as well.

Results and Discussion

1. Methodology

The high-precision CBS-Q[26] and G3[27] methods yield bond energies with mean absolute deviations (MAD) of only 0.80 and 0.96 kcal on the G2/97 test set of molecules.[28,29] The multimethod approach of the CBS-Q and G3 methods specifically addresses basis set truncation effects, electron–electron correlation effects, configuration interaction effects, and the empirically known shortcomings of the different computational methods through appropriate scaling. The obtained energies have error margins that are usually as good as and frequently better than experimental energies and consistently superior to those of all single-method approaches (DFT methods included). Not surprisingly, these methods are the tool of choice wherever experimental energies are not available, in conflict with each other, or of dubious quality. One of the less obvious advantages of the CBS-Q and G3 approach lies in the fact that both methods operate with a fixed choice of basis sets. The absence of basis set ambiguity and the well-established error margins of the methods allow for a direct comparison of the CBS-Q and G3 data. A notable early success validating the superior quality of the CBS-Q approach was the excellent accuracy obtained for the elementary steps involved in the destruction of ozone by chlorine radicals, for which all previous methods had resulted in errors of 20 kcal and more.[54,55] Due to the unfavorable scaling of their QCISD(T) step, the use of the CBS-Q and G3 methods is at present rarely practical for molecules with more than 8–10 non-hydrogen ("heavy") atoms. A second limitation is the fact that both methods are currently implemented[30] only for main group elements of the first two (G3) or three (CBS-Q) long periods. A large part of the periodic table is thus at present closed to high-precision compound calculations and remains the domain of single-method calculations in general and DFT methods in particular.

While older, commonly used DFT methods[31,32] are known to produce thermochemical errors of 20 kcal mol^{-1} or more in unfavorable cases,[54] DFT methods developed in the last decade have significantly lower error margins.[33–39] The quest for improved thermochemical accuracy continues to be one of the major driving forces behind the development of new DFT methods.[36–39] High-precision methods like the CBS-Q and G3 have played a crucial role, as they provide thermochemical benchmark values for the assessment of new DFT methods that exceed experimental data in number and often quality.

A typical example is the Boese–Martin hybrid DFT method (BMK method), which has been benchmarked with high-precision W1 calculations and is the first DFT method that approaches the accuracy of CBS-Q and G3 data even for challenging molecules like those found in the G2/97 test set.[39]

Despite their deceptively simple structure, disulfanes are known to be unusually challenging for DFT calculations[40,41] and are accordingly a good test case to study the accuracy of newer DFT methods.

2. Previous High-Precision Calculations

A limited number of sulfur–sulfur bond energies have been examined with older high-precision thermochemical methods. The bond energies of five disulfanes have been examined with the CBS-4m method by Benassi and Taddei,[42] who noted the deficiencies of the method and introduced a modified CBS-4 procedure (CBS-4D/E) that delivers improved accuracy.

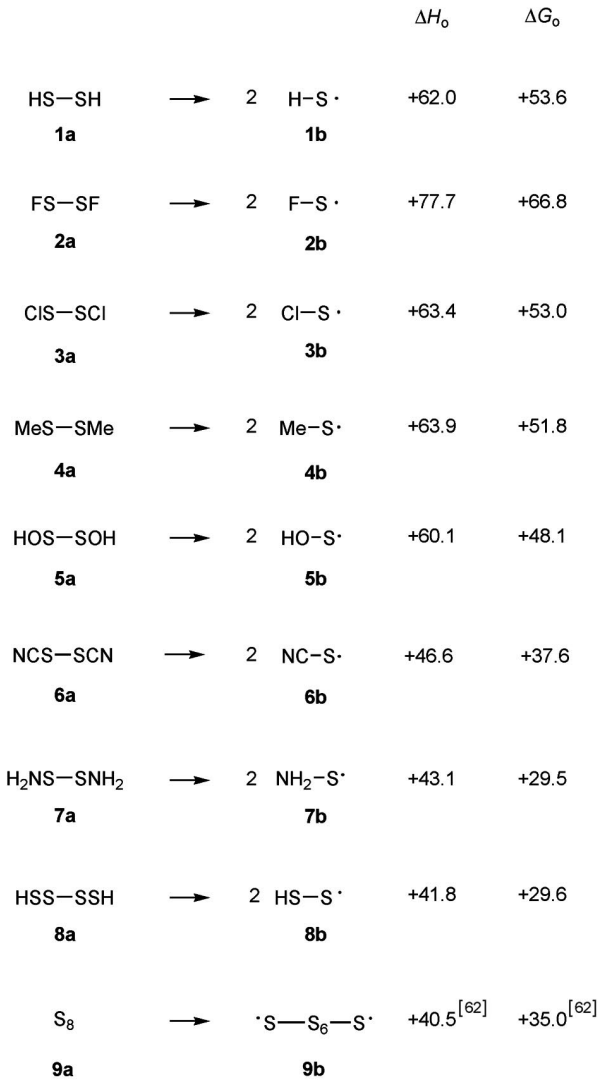
For disulfane, H_2S_2, bond energies of 64.7 and 61.8 kcal mol^{-1} were obtained at the G2(MP2) and CBS-Q levels,[43] very similar to the CBS-Q value for dimethyldisulfane of 64.2 kcal.[44]

State-of-the-art CBS-Q and G3 energies for disulfanes HSSH, ClSSCl, and FSSF were obtained by Y. Fu et al. while this study was in progress. Their bond energies differ significantly from some of the previously published experimental values.[45] To the best of our knowledge, the sulfur–sulfur bond energy in S_8 has not previously been studied with the CBS-Q, G3, or similarly accurate methods.[46] CBS-4m data for S_8 were used in our own study on thioureas.[24]

3. This Study – Bond Energies of Sulfur (S_8) and Disulfanes through CBS-Q, G3, and DFT Calculations

In this study, high-precision CBS-Q[26] and G3 calculations[27] are used to determine the sulfur–sulfur bond energies in elemental sulfur, S_8, and representative disulfanes X–S–S–X (X = H, F, Cl, OH, NH_2, CH_3, and CN). The high-precision energies are then used to compare the accuracy of older hybrid DFT methods like the B3LYP method[32] with newer methods recommended for thermochemical calculations: specifically the MPW1PW91,[33] B1B95,[34] B98,[35] MPW1B95,[36–38] BB1K,[36–38] MPWB1K,[36–38] and BMK[39] methods. As the CBS-Q and G3 methods use a slightly different approach but are of very similar accuracy, arithmetic averages of the CBS-Q and G3 energies are used as benchmark data (Scheme 3).

Individual CBS-Q and G3 energies are listed in Table 1, together with the respective sulfur–sulfur bond lengths and valence vibration frequencies. To ensure a reasonable degree of basis set convergence, the DFT calculations were carried out with two large basis sets: 6-311G(2d,p) and 6-311G(3df,p).



Scheme 3. Bond energies (averages of CBS-Q and G3 values) of selected disulfanes, tetrasulfane, and S_8.

The term "bond energy" is frequently used in a rather loose fashion, and it is often not clear if quoted values refer to "energies" in the narrow sense ($\Delta E°$), or enthalpies ($\Delta H°$), or even free energies, $\Delta G°$. The bond energies most commonly listed in standard reference manuals are in fact bond dissociation energies (BDE) at 298.15 K (D_o). Unfortunately, this can be another source of confusion, as, notwithstanding the name, bond dissociation energies are defined as enthalpies. The calculations carried out in this study yield all relevant energies for the bond dissociation: energies at 0 K (ΔE_o), energies at 298.15 K ($\Delta E°$), enthalpies at 298.15 K (BDE, D_o, $\Delta H°$), Gibbs free energies ($\Delta G°$), and – as the difference between $\Delta H°$ and $\Delta G°$ – entropies ($\Delta S°$). For the remainder of this discussion, the term "bond energy" is understood to refer to bond dissociation energies, D_o, at 298.15 K, which are defined as enthalpies, $\Delta H°$.

All calculations were carried out with the Gaussian 03 Rev. D suite of programs.[30] Optimized structures were verified to correspond to local minima through frequency calculations. The lowest frequencies are listed in the Support-

Table 1. Sulfur–sulfur bond energies (in kcal mol^{-1}), S–S valence vibrations (ν), and sulfur–sulfur distances (d_{SS}, in pm) of disulfanes and S_8 at the CBS-Q and G3 levels (T = 298.15 K).

X	Method	E_o	$\Delta E°$	$\Delta H°$	$\Delta G°$	$T\Delta S°$	d_{SS}	ν(S–S)
HSSH	G3	60.23	61.02	61.61	52.23	9.39	206.94	568
	CBS-Q	62.94	63.76	64.32	54.94	9.41	207.07	569
FSSF	G3	75.69	75.80	76.93	65.84	10.56	192.26	611
	CBS-Q	77.67	77.80	78.38	67.78	10.61	192.53	611
ClSSCl	G3	61.90	61.75	62.34	52.01	10.33	197.83	570
	CBS-Q	63.95	63.82	64.41	53.99	10.43	198.05	570
MeSSMe	G3	62.55	62.45	63.07	50.82	12.25	205.36	557
	CBS-Q	64.24	64.18	64.78	52.85	11.93	205.50	557
HOSSOH	G3	58.40	58.65	59.24	47.33	11.91	199.04	585
	CBS-Q	60.03	60.32	60.91	48.92	11.99	199.39	585
NCSSCN	G3	45.97	46.00	46.59	37.56	9.03	208.45	567
	CBS-Q	45.98	46.03	46.62	37.53	9.09	208.50	566
H_2NSSNH_2	G3	41.23	42.07	42.66	29.02	13.64	206.72	539
	CBS-Q	42.02	42.90	43.49	29.99	13.50	207.10	538
HSS–SSH[a]	G3	40.93	40.79	41.38	29.14	12.23	206.46	523
	CBS-Q	41.81	41.70	42.30	29.97	12.33	206.60	523
S_8[b]	G3	39.48	40.28	40.28	34.77	5.51	206.62	508–576
	CBS-Q	39.96	40.78	40.78	35.29	5.49	206.77	508–575
S_8[c]	G3	41.02	41.83	41.83	36.09	5.74	206.62	518–546
	CBS-Q	41.59	42.42	42.42	36.70	5.74	206.77	518–546

[a] Central S–S bond. [b] Ring opening to primary diradical. [c] Ring opening to secondary (helical) diradical.

ing Information. For DFT calculations, the zero-point vibrational energies (ZPE) were included without scaling. Energies were converted from Hartree to kcal mol^{-1} with the conversion factor of 1 Hartree = 672.51 kcal.

Starting Geometries

For disulfanes, XSSX, the presence of substituents with less than total rotational symmetry (OH, NH_2, SH, CH_3) leads to a set of rotamers with similar energies. The rotamers with the lowest energies were identified through comparison of their respective CBS-Q and G3 energies. All bond energies in this study refer to the rotamers with the lowest CBS-Q/G3 energy. The most stable rotamer is not necessarily the one with the highest symmetry: while HOSSOH can exist in three distinct rotameric forms, the two isomers with point group C_2 were found to be higher in energy than the isomer possessing only C_1 symmetry. For the SCN radical, the linear geometry represents a bona fide local minimum as well (absence of virtual frequencies) but is higher in energy for all methods employed in this study.

Two different rotamers were examined for the ring opening of S_8 (**9a**). While the immediate product of the ring opening of S_8 is the diradical **9b**, rotation around the central S(4)–S(4′) bond leads to a secondary diradical **9b′**. At the CBS-Q and G3 levels, **9b′** was found to be slightly higher in energy ($\Delta G°$ = +1.4 kcal) than **9b** (Scheme 4).

The high-precision bond energies (Table 1 and Scheme 3) confirm a surprising variability in the strength of the sulfur–sulfur bond with bond energies ($\Delta H°$) ranging from a maximum value of 77.7 kcal mol^{-1} (S_2F_2) to only 41.8 kcal mol^{-1} in tetrasulfane, HSSSSH.

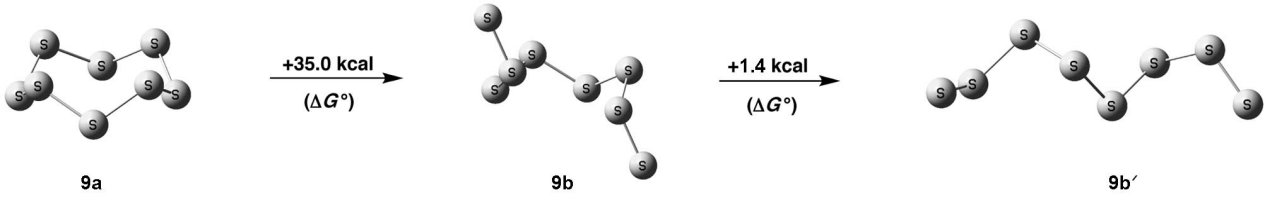
The bond energy of elemental sulfur (40.5 kcal) marks the low end of the range and is in any case much lower than the generic literature values of 54 kcal mol^{-1} or 64 kcal mol^{-1}[15,16] Surprisingly, the value for S_8 also does not agree well with the value of 32.8 kcal mol^{-1} favored by Benson's critical review[17] or the value of 27.5 ± 5 kcal obtained by Powell and Eyring for the formation of *catena*-sulfur from S_8.[19] The discrepancies between the calculated bond energy for S_8 and the value favored by Benson may reflect effects of the condensed phase on the dissociation energy but could also point to the operation of thermal processes other than the simple monomolecular ring opening to the respective diradicals **9b** or **9b′**. Other potential error sources for the experimental value would include the presence of impurities like water, air, or the presence of small amounts of other sulfur allotropes like S_7 or S_9.[5] The kinetic effect of impurities has been documented in a study by Bartlett et al., who found that S_6 is stable at 65 °C for extended periods of time, but converts rapidly to S_8 upon the addition of amines.[5b]

To put into perspective just how low a value of 40.5 kcal for the bond energy of S_8 really is, we note that it is only slightly higher than that of iodine, I_2, (36 kcal),[16] a textbook case for a weak nonmetal bond.

While S_8 has the lowest sulfur–sulfur bond energy of all compounds investigated in this study, this is not sufficient to also make it the best thermal source of sulfur radicals (Scheme 3).

The reason for this discrepancy is entropic. While the rupture of the sulfur–sulfur bond is entropically favored for all of the investigated compounds, the entropy gain, $T\Delta S°$, for the ring opening of S_8 is only 5.5 kcal mol^{-1} but 9.4 to 13.6 kcal mol^{-1} for the dissociation of disulfanes XSSX into radicals XS$^{\cdot}$ (Table 1). The difference reflects the fact that dissociation of disulfanes creates two independent molecules XS$^{\cdot}$, while ring opening of the sulfur ring creates only one, the tethered diradical **9b** or its rotamer **9b′**.

The homolytic dissociation of disulfanes XSSX into radicals XS$^{\cdot}$ is thus more facile than the bond energies would suggest with standard Gibbs energies, $\Delta G°$, ranging from



Scheme 4.

66.8 kcal mol^{-1} (X = F) to only 29.5 kcal mol^{-1} (X = NH_2). Diaminodisulfanes and tetrasulfanes are accordingly the best thermal source of sulfur radicals among the investigated compounds, slightly better than S_8 itself.

Trends in Bond Energies

Despite the strong variation in the strength of the sulfur–sulfur bond (Scheme 3, Table 1), there is no obvious correlation with the respective sulfur–sulfur bond lengths (Table 1, Table 4). While FSSF, the disulfane with the strongest sulfur–sulfur bond, does show the shortest sulfur–sulfur bond, no such correlation exists for the disulfanes HSSH, MeSSMe, and ClSSCl, all of which have very similar bond energies but quite different bond lengths.

The influence of the substituent X on the sulfur–sulfur bond energies in the disulfanes XSSX follows the order F > H ≈ CH_3 ≈ Cl > OH > CN > NH_2 > SH, which is not readily rationalized by the typical inductive and mesomeric effects of the substituents X.

DFT Calculations and Sulfur–Sulfur Bond Energies

With the high-precision CBS-Q and G3 bond energies (arithmetic average of enthalpies) as benchmark values, the thermochemical accuracy of different DFT methods was investigated at the DFT/6-311G(2d,p) and DFT/6-311G(3df,p) levels.

The average errors show that the DFT/6-311G(3df,p) enthalpies (Table 2) are more accurate (≈ 1 kcal) than the respective DFT/6-311G(2d,p) energies (Table 3). This improvement is small if expressed as a percentage of the respective bond energies but actually quite large if expressed as a percentage of the average errors. More significant than the choice of either of the two basis sets is the choice of the DFT method itself.

Comparison of the B3LYP data (largest errors) with the BMK data (smallest errors) shows a reduction in the maximum error from 11.4 to 3.7 kcal at no additional computational cost.

The ranking of the relative accuracy of the different DFT methods depends on the basis set employed and whether average or maximum errors are used. Using the maximum errors of the more accurate DFT/6-311G(3df,p) bond energies, the thermochemical accuracy of the DFT methods increases as B3LYP < B1B95 < B98, MPW1PW91, MPW1B95 < BB1K < MPWB1K < BMK. The use of average errors leads to a slightly different order: B3LYP < B98 < B1B95, MPW1PW91 < MPW1B95, BB1K < MPWB1K < BMK.

Irrespective of the type of error or basis set employed, the B3LYP energies show the largest error, the MPWB1K and BMK data the smallest. As the most accurate DFT methods used in this study (MPW1B95, BB1K, MPWB1K, and BMK) show deviations from the CBS-Q and G3 data that are comparable to the error margins of the CBS-Q and G3 methods, it is prudent to regard them as similarly accurate until significantly more precise reference data – computational or experimental – become available.

The high accuracy of the MPW1B95, BB1K, MPWB1K, and BMK methods recommends these methods for thermochemical calculations involving heavier main group elements, provided that large basis sets like the 6-311G(3df,p) basis are applied. In view of the large error margins (up to 10 kcal), the use of B3LYP calculations for thermochemical studies of heavy main group compounds cannot be justified.

Table 2. Sulfur–sulfur bond energies $\Delta H°$ (in kcal mol^{-1}) of disulfanes XSSX and elemental sulfur, S_8, at the DFT/6-311G(3df,p) level. Errors vs. high-precision CBS data (arithmetic average of CBS-Q and G3 values) in italics.

X:	H	F	Cl	CH_3	OH	NH_2	CN	HS[a]	S_8[b]	S_8[c]	Average error	Maximum error
CBS	62.96	77.65	63.38	63.93	60.08	43.09	46.61	41.84	40.53	42.13		
B3LYP	59.38	73.64	57.66	55.87	53.85	34.66	35.75	32.72	32.44	30.72		
	3.58	*4.01*	*5.72*	*8.06*	*6.23*	*8.43*	*10.85*	*9.12*	*8.09*	*11.42*	*7.56*	*11.42*
B98	63.33	76.32	60.84	59.71	57.00	38.28	39.39	36.97	36.31	34.92		
	0.37	*1.33*	*2.54*	*4.22*	*3.08*	*4.81*	*7.22*	*4.87*	*4.22*	*7.21*	*3.99*	*7.22*
B1B95	65.69	80.02	62.30	62.30	59.68	39.50	41.58	37.26	35.78	34.27		
	2.73	*2.37*	*1.09*	*1.63*	*0.40*	*3.59*	*5.03*	*4.58*	*4.75*	*7.86*	*3.40*	*7.86*
MPW1PW91	62.82	78.10	61.11	59.84	58.52	39.07	39.66	36.74	36.81	34.94		
	0.14	*0.45*	*2.27*	*4.09*	*1.56*	*4.02*	*6.95*	*5.10*	*3.72*	*7.19*	*3.55*	*7.19*
MPW1B95	66.51	80.58	62.98	63.35	60.58	40.48	42.63	37.94	36.32	34.96		
	3.55	*2.93*	*0.40*	*0.58*	*0.50*	*2.61*	*3.98*	*3.90*	*4.21*	*7.17*	*2.98*	*7.17*
BB1K	64.67	78.12	61.00	61.90	59.15	39.39	46.00	37.53	37.60	36.04		
	1.71	*0.47*	*2.38*	*2.03*	*0.93*	*3.70*	*0.61*	*4.30*	*2.93*	*6.10*	*2.51*	*6.10*
MPWB1K	65.30	78.71	61.68	62.81	59.94	43.85	42.74	38.47	37.90	36.49		
	2.34	*1.06*	*1.70*	*0.58*	*0.13*	*0.76*	*3.87*	*3.37*	*2.63*	*5.64*	*2.21*	*5.64*
BMK	66.22	76.00	62.60	65.85	58.19	39.37	44.40	42.03	42.63	42.03		
	3.26	*1.65*	*0.78*	*1.91*	*1.89*	*3.71*	*2.22*	*0.19*	*2.10*	*0.10*	*1.78*	*3.71*

[a] Internal sulfur–sulfur bond. [b] Primary S_8 diradical **9b**. [c] Secondary S_8 diradical **9b′**.

Table 3. Sulfur–sulfur bond energies $\Delta H°$ (in kcal mol^{-1}) of disulfanes XSSX and elemental sulfur, S_8, at the DFT/6-311G(2d,p) level. Errors vs. high-precision CBS data (arithmetic average of CBS-Q and G3 values) in italics.

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B3LYP	57.89	70.82	56.67	54.28	51.68	33.98	35.22	32.68	31.76	30.16		
	5.08	*6.82*	*6.71*	*9.65*	*8.41*	*9.11*	*11.38*	*9.16*	8.77	*11.97*	*8.71*	*11.97*
B98	62.05	74.06	59.91	58.26	55.18	37.72	38.91	36.74	35.35	34.12		
	0.92	*3.59*	*3.47*	*5.67*	*4.90*	*5.37*	*7.70*	*5.10*	5.18	*8.01*	*4.99*	*8.01*
B1B95	61.46	75.60	60.13	58.30	56.49	38.35	40.80	36.41	36.21	34.57		
	1.51	*2.05*	*3.25*	*5.63*	*3.59*	*4.74*	*5.81*	*5.43*	4.32	*7.56*	*4.39*	*7.56*
MPW1PW91	62.86	74.98	59.53	59.84	56.57	38.21	39.17	36.82	36.83	35.62		
	0.11	*2.68*	*3.85*	*4.09*	*3.51*	*4.88*	*7.44*	*5.02*	3.70	*6.51*	*4.18*	*7.44*
MPW1B95	64.09	77.10	61.10	60.39	57.23	38.50	41.80	36.67	35.54	33.86		
	1.12	*0.55*	*2.28*	*3.54*	*2.85*	*4.59*	*4.81*	*5.17*	4.99	*8.27*	*3.82*	*8.27*
BB1K	64.75	77.58	61.72	61.39	58.08	39.40	41.00	37.74	35.64	34.54		
	1.78	*0.07*	*1.66*	*2.54*	*2.00*	*3.69*	*5.10*	*4.10*	4.89	*7.59*	*2.32*	*7.59*
MPWB1K	63.49	75.51	60.16	60.71	57.28	38.99	41.82	37.72	37.30	36.06		
	0.52	*2.14*	*3.22*	*3.22*	*2.80*	*4.10*	*4.79*	*4.12*	3.26	*6.07*	*3.42*	*6.07*
BMK	65.00	74.84	61.86	64.66	57.62	39.42	44.56	40.58	40.49	39.73		
	2.03	*2.81*	*1.52*	*0.73*	*2.45*	*3.67*	*2.05*	*1.26*	0.04	*2.40*	*1.90*	*3.67*

[a] Internal sulfur–sulfur bond. [b] Primary S_8 diradical **9b**. [c] Secondary S_8 diradical **9b′**.

Computational Structures of Disulfanes XSSX and S_8

The computational sulfur–sulfur distances at the DFT/6-311G(3df,p) level are generally shorter by ca. 2 pm than those obtained at the DFT/6-311G(2d,p) level. This difference is not negligible, and it must be concluded that the DFT/6-311G(2d,p) structures are not converged.[56] A discussion of structural accuracies should accordingly be based on DFT/6-311G(3df,p) data.

Experimental gas phase structures which should compare particularly well to computational data are available for most disulfanes. However, some of the structural data are in disagreement with each other, so it is difficult to rank the accuracy of the computational structures (Table 4).

We therefore begin our brief assessment of the structural accuracy of the different DFT methods with the structure of sulfur itself, which has been repeatedly studied through single-crystal X-ray studies that agree well with each other, regardless of the sulfur modification.[52]

At the DFT/6-311G(3df,p) level, the experimental bond lengths of 204.5–204.8 pm obtained from single-crystal X-ray diffraction studies of α-S_8,[52a] β-S_8,[52b] and γ-S_8[52c] are reproduced accurately only by the MPW1PW91 and B1B95 methods, while the remaining methods give bond lengths that are either too long (B3LYP, B98, BMK) or too short (MPW1B95, BB1K, MPWB1K). The same trend in accuracy is observed for the respective disulfane bond lengths. The MPW1PW91 and B1B95 methods are the best choice as far as structures are concerned, provided that the rather unwieldy 6-311G(3df,p) basis set can be employed. (Table 1).

The MPW1PW91/6-311G(3df,p) and B1B95/6-311G(3df,p) levels should accordingly allow accurate predictions for the unknown structures of the S_8 diradicals **9b** and **9b′** (Table 5).

Irrespective of the DFT method employed, the structures of the diradicals **9b** and **9b′** share a number of peculiarities. They display a distinct pattern of alternating short and long bond lengths starting with rather short terminal sulfur–sulfur bonds.

While the CBS-Q and G3 structures of **9b** and **9b′** are helical[53] with dihedral angles close to 90°, the DFT structures show the four terminal sulfur atoms S(1)–S(2)–S(3)–S(4) in a nearly coplanar arrangement. The proximity of the nonbonded S(1) and S(4) atoms may indicate a weak S(1)–S(4) bonding interaction.

Like the terminal bonds in the diradicals **9b** and **9b′**, the S–X bond lengths in the radicals are shortened significantly (4–7 pm) relative to those in the respective disulfanes. The notable exceptions are the radicals HS$^{\cdot}$ and MeS$^{\cdot}$, for which the X–S bond lengths are essentially identical to those of disulfanes HSSH and MeSSMe.

The observed pattern of bond shortening is consistent with partial multiple bonding in the radicals XS$^{\cdot}$ (2-center-3-electron bonding) for the π-donor groups X = F, Cl, OH, NH_2, and SH. For NCS$^{\cdot}$, multiple bonding can be attributed to delocalization into the CN π*-orbitals. While a comprehensive analysis of substituent effects in disulfanes is beyond the scope of this study, it is important to note the that radicals can be stabilized by both π-donors and π-acceptors[61] Dissociation of dicyanodisulfane, NCS–SCN, into the spin-delocalized SCN radical with the π-acceptor –CN is accordingly facile as well: $\Delta H°$ = +46.6 kcal, $\Delta G°$ = 37.6 kcal (both arithmetic averages of CBS-Q and G3 data).

The spin delocalization operating in the sulfur radicals X–S$^{\cdot}$ is readily quantified by examining the spin densities on sulfur and the adjacent atom in the substituents X. Table 6 gives the respective Mulliken atomic spin densities arranged in decreasing spin density on sulfur. Atoms in

Table 4. Structural parameters of selected disulfanes XSSX. Experimental data from gas phase electron diffraction (ED), microwave (MW) or single-crystal X-ray (XRD) studies. Calculated parameters at the DFT/6-311G(2d,p) level (left of double columns) and DFT 6-311G(3df,p) level (right of double columns). DFT bond lengths of radicals X–S· (last column) are given for comparison. For the structures of S_8 and diradicals **9b** and **9b′**, see Table 5.

X	Method	S–S		X–S		X–S–S		X–S–S–X		X–S·	
H	MW[47a]	206.10(3)		134.21(5)		91.3(5)		90.60(5)		–	
	ED[47b]	206.11(1)		134.10(3)		97.42(40)		90.75(50)		–	
	B3LYP	209.66	207.26	134.79	134.82	98.19	98.65	90.72	90.51	134.81	134.75
	B98	209.46	207.57	134.87	134.86	98.10	98.50	90.79	90.77	134.88	134.81
	MPW1PW91	206.91	204.78	134.11	134.55	98.08	98.70	90.81	90.59	134.46	134.41
	B1B95	206.43	204.32	134.27	134.31	98.08	98.57	90.87	90.55	134.25	134.22
	MPW1B95	206.18	204.07	134.11	134.16	98.08	98.56	90.77	90.57	134.11	134.09
	BB1K	205.34	203.27	133.62	133.68	98.16	98.60	90.69	90.50	133.66	133.65
	MPWB1K	205.18	203.13	133.52	133.59	98.16	98.53	90.70	90.60	133.58	133.56
	BMK	208.76	208.30	135.15	135.03	97.93	98.11	90.97	90.76	135.29	135.23
	CBS-Q/G3[a]	207.07	206.94	134.37	134.37	99.03	99.05	90.39	90.37	134.44	134.44
F	ED[48a]	189.0(2)		163.5(2)		108.3(2)		87.7(4)		–	
	MW[48b]	188.8(10)		163.5(10)		108.3(5)		87.9(15)		–	
	B3LYP	192.52	190.21	166.72	165.04	108.62	108.75	88.70	87.76	162.30	160.95
	B98	193.07	191.16	165.76	163.92	108.46	108.51	88.62	87.67	161.61	160.21
	MPW1PW91	190.80	188.80	164.99	163.30	108.62	108.70	88.62	87.73	160.95	159.63
	B1B95	190.30	188.32	164.64	162.95	108.45	108.53	88.69	87.80	160.63	159.35
	MPW1B95	190.26	188.25	164.05	162.42	108.37	108.35	88.69	87.80	160.23	158.97
	MPWB1K	190.00	187.87	162.34	160.84	107.67	107.89	88.57	87.70	159.06	157.84
	BB1K	190.02	187.97	162.70	161.17	107.80	107.99	88.58	87.69	159.32	158.08
	MPWB1K	189.98	187.87	162.38	160.84	107.67	107.89	88.46	87.70	159.06	157.84
	BMK	194.51	194.60	163.91	162.13	107.55	107.33	88.85	87.66	160.62	159.25
	CBS-Q/G3[a]	192.53	192.26	166.12	165.66	106.74	106.64	89.07	88.92	162.91	162.68
CH_3	MW[49a]	203.8		181.10		102.8		84.7		–	
	ED[49b]	202.9 ± 0.3		181.6 ± 0.3		103.2 ± 0.2		85.3 ± 3.7		–	
	B3LYP	207.82	205.32	183.29	182.34	103.42	103.96	87.29	87.32	180.76	179.72
	B98	207.80	205.73	183.41	182.57	103.20	103.66	87.11	87.05	180.86	179.99
	MPW1PW91	205.33	203.06	181.46	180.65	103.21	103.79	86.22	86.94	179.15	178.25
	B1B95	204.81	202.56	181.08	180.28	102.69	103.30	85.20	86.04	178.63	177.71
	MPW1B95	204.55	202.35	180.79	179.96	102.55	103.04	85.48	84.90	178.40	177.51
	MPWB1K	203.65	201.49	179.90	179.11	102.39	102.88	85.04	84.86	177.93	177.05
	BB1K	203.80	201.64	180.11	179.31	102.53	103.00	85.71	85.09	178.01	177.14
	BMK	207.41	206.93	183.32	183.15	102.05	102.70	86.09	86.88	181.25	180.98
	CBS-Q/G3[a]	205.50	205.36	181.62	181.19	101.95	102.13	84.67	85.10	180.31	179.92
Cl	ED[50a]	193.1(5)		205.7(20)		108.2(3)		84.8(13)	–		
	MW[50b]	195.04(12)		205.52(7)		107.66(5)		85.24(10)	–		
	X-ray[50c]	194.3(1)		–		107.1(1)		84.8(10)	–		
	B3LYP	196.44	194.68	212.43	209.87	109.27	109.39	87.21	86.82	202.09	199.41
	B98	197.24	195.86	211.04	208.81	108.89	108.96	86.91	86.50	201.61	199.37
	MPW1PW91	195.35	193.84	208.54	206.10	108.82	108.90	86.84	86.36	199.53	197.08
	B1B95	194.93	193.47	208.14	205.66	108.54	108.59	86.67	86.13	199.04	196.59
	MPW1B95	194.95	193.46	207.56	205.09	108.24	108.34	86.43	86.03	198.78	196.34
	MPWB1K	195.03	193.58	205.57	203.12	107.43	107.54	86.12	85.50	197.89	195.44
	BB1K	195.02	193.53	205.90	203.47	107.65	107.76	86.32	85.71	198.04	195.60
	BMK	199.14	199.63	208.28	206.68	107.15	107.24	85.81	85.44	201.00	199.73
	CBS-Q, G3[a]	198.05	197.83	207.21	207.18	107.49	107.49	85.82	85.82	199.97	200.00
HO	X-ray[51]	197.2(1)[b]		165.8(4)[b]		108.2(1)[b]		81.5(1)[b]		–	
	ED[51]	196.0(3)[b]		165.3(3)[b]		108.2(3)[b]		91(4)[b]		–	
	B3LYP	200.85	198.03	169.09	167.28	108.09	108.48	87.54	86.90	165.20	163.89
	B98	201.21	198.98	168.26	166.87	107.97	108.04	87.68	86.82	164.57	163.23
	MPW1PW91	198.54	196.07	167.39	166.18	108.04	108.15	87.44	86.85	163.70	162.49
	B1B95	198.01	195.57	167.34	165.36	107.83	108.24	87.43	86.84	163.39	162.24
	MPW1B95	197.83	196.07	166.25	166.18	107.52	108.15	87.53	86.85	163.00	161.87
	MPWB1K	198.33	194.78	165.43	163.76	106.57	107.73	86.86	86.54	161.75	160.67
	BB1K	197.33	194.90	165.08	163.78	107.47	107.79	87.05	86.47	161.99	160.91
	BMK	201.81	201.64	166.40	164.38	107.35	107.47	87.26	86.54	163.04	161.50
	CBS-Q, G3[a]	199.39	199.04	168.83	169.12	106.47	106.31	86.65	86.48	165.51	165.46
CN	B3LYP	211.91	209.70	170.27	169.32	101.66	102.19	89.75	88.74	163.43	162.51
	B98	211.49	209.83	170.43	169.47	101.47	101.96	89.74	88.82	163.48	162.63
	MPW1PW91	208.75	206.88	169.42	168.52	101.34	101.86	89.86	88.88	162.59	161.82
	B1B95	208.14	206.31	169.24	168.33	101.09	101.63	89.89	88.90	162.42	161.58
	MPW1B95	207.76	205.85	169.11	168.26	100.97	101.52	89.68	88.66	162.33	161.53
	MPWB1K	206.36	204.48	168.80	167.99	100.78	101.35	89.52	88.57	162.10	162.10
	BB1K	206.58	204.71	168.89	168.08	100.87	101.43	89.70	88.76	162.16	164.90
	BMK	209.70	209.53	171.09	169.94	100.72	101.21	90.08	88.74	164.39	164.90
	CBS-Q, G3[a]	208.50	208.45	170.35	169.91	100.62	100.79	85.93	86.55	167.38	167.38
NH_2	B3LYP	210.06	207.45	171.10	169.58	110.21	110.43	89.04	88.61	164.69	163.74
	B98	209.80	207.83	170.84	169.23	110.09	110.28	88.99	88.62	164.34	163.39
	MPW1PW91	206.82	204.51	169.72	168.30	110.00	110.19	88.91	88.40	163.42	162.55
	B1B95	206.19	203.89	169.48	168.01	109.76	110.05	83.42	88.49	163.23	162.39
	MPW1B95	205.82	203.56	169.11	167.69	109.59	109.81	88.65	88.26	162.97	162.15
	MPWB1K	204.52	202.33	168.10	166.71	109.16	109.41	88.39	88.84	162.12	161.34
	BB1K	204.76	202.56	168.31	166.92	109.30	109.54	88.61	88.04	162.29	161.50
	BMK	208.71	208.66	169.99	167.66	109.32	109.54	89.11	88.15	163.17	161.98
	CBS-Q, G3[a]	207.10	206.72	170.17	170.44	109.16	109.04	87.28	87.07	164.32	164.30
HS	B3LYP	208.88	206.67	209.71	207.45	107.81	108.19	86.32	86.90	200.12	197.64
	B98	208.89	206.98	209.38	207.67	107.52	107.85	85.70	86.08	200.24	198.26
	MPW1PW91	206.37	204.44	206.93	204.88	107.48	107.79	85.88	86.20	197.91	195.72
	B1B95	205.88	203.89	206.38	204.38	107.15	107.42	85.80	85.94	197.45	195.27
	MPW1B95	205.55	203.63	206.08	204.06	106.90	107.15	85.07	85.18	197.23	195.06
	MPWB1K	204.59	202.66	204.95	202.95	106.43	105.73	84.08	84.24	196.43	194.34
	BB1K	204.75	202.86	205.14	203.14	106.61	106.91	84.71	84.85	196.55	194.37
	BMK	207.99	207.53	208.52	208.10	106.36	106.82	83.51	84.61	200.45	200.16
	CBS-Q, G3[a]	206.60	206.46	206.84	206.71	107.09	107.05	82.16	82.10	198.28	198.11

[a] G3 structures are at the MP2(full)/6-31G(d) level, CBS-Q structures at the MP2(FC)/6-31G(d′) level. [b] MeOSSOMe as substitute structure for the unknown structure of HOSSOH.

Table 5. Selected bond lengths and angles of the S_8 diradicals **9b** and **9b′** at the DFT/6-311G(3df,p) level. CBS-Q and G3 data are presented for comparison. Suggested best values are in italics. Last column: experimental (X-ray data) and computational S–S bond lengths in elemental sulfur, S_8.

Method	S1–S2	S2–S3	S3–S4	S4–S5	S1–S4	S1–S2–S3–S4	S_8
Exp.	–	–	–	–	–	–	204.6(3) [52a] 204.5(2) [52b] 204.8(2) [52c]
B3LYP[a]	192.36	222.22	201.38	212.58	351.92	20.67	207.24
B3LYP[b]	192.04	224.92	200.11	213.22	340.75	7.02	207.24
B98[a]	193.21	220.07	202.54	211.57	351.66	23.41	207.44
B98[b]	192.92	222.41	201.30	212.07	338.58	11.31	207.44
MPW1PW91[a]	*191.24*	*216.12*	*200.42*	*208.36*	*348.76*	*27.73*	*204.76*
MPW1PW91[b]	*190.77*	*219.23*	*198.94*	*209.01*	*331.72*	*12.14*	*204.76*
B1B95[a]	*190.34*	*217.63*	*199.07*	*208.68*	*334.40*	*15.78*	*204.16*
B1B95[b]	*190.51*	*218.19*	*198.72*	*208.16*	*326.88*	*15.57*	*204.16*
MPW1B95[a]	190.17	216.80	199.03	207.96	333.71	15.99	203.85
MPW1B95[b]	190.40	217.11	198.73	207.55	326.48	16.16	203.85
BB1K[a]	189.84	213.47	199.11	205.76	335.94	22.76	202.94
BB1K[b]	190.00	214.08	198.71	205.85	328.19	21.08	202.94
MPW1B1K[a]	189.76	212.93	199.08	205.39	335.81	23.54	202.76
MPW1B1K[b]	189.95	213.47	198.70	205.55	328.06	22.16	202.76
BMK[a]	196.22	216.27	205.41	210.03	356.68	34.53	207.64
BMK[b]	196.33	215.11	205.20	209.38	352.12	33.61	207.64
G3[a]	195.61	211.68	205.96	207.07	409.52	77.27	206.62
G3[b]	195.38	211.71	205.58	207.53	401.06	71.56	206.62
CBS-Q[a]	195.81	211.77	206.09	207.22	409.85	76.96	206.77
CBS-Q[b]	195.62	211.76	205.77	207.64	403.10	72.48	206.77

[a] Primary diradical **9b**. [b] Secondary diradiacal **9b′**.

Table 6. Mulliken spin densities[59] and AIM bond orders (BO)[59] of selected sulfur radicals (XS·) and diradicals (·S–S_6–S·) at the MPWB1K/6-311G(2d,p) level.

X	X–*S*[a]	X–*S*[b]	*X*–S[a]	*X*–S[b]	BO[c]
MeS	0.978	0.940	0.038	0.005	1.25
FS	0.921	0.893	0.079	0.107	1.19
ClS	0.875	0.847	0.125	0.153	1.59
HOS	0.839	0.817	0.169	0.187	1.39
CN	0.785	0.739	0.194	0.122	1.63
NH_2S	0.720	0.706	0.312	0.306	1.58
HSS	0.722	0.695	0.291	0.305	1.81
S_8 (9b)	0.602	–	0.372	–	–
S_8 (9b′)	0.598	–	0.370	–	–

[a] Mulliken spin densities. [b] AIM spin densities. [c] AIM bond orders.

molecules (AIM) spin densities[59] and bond orders[59] are given for comparison.

The Mulliken spin densities on sulfur decrease rather smoothly along the series Me < F < Cl < OH < CN < NH_2 < SH and reach a minimum of ca. 60% in the S_8 diradicals **9b** and **9b′**.

The order of increasing spin delocalization in the sulfur radicals XS· is essentially that of the S–S bond energies. It is therefore likely that spin delocalization in XS· is a significant factor in the strong variation of the sulfur–sulfur bond energy.[60] A number of the radicals show structural details that are important in the context of spin delocalization. The radical NH_2S· was found to be planar at all levels of theory employed in this study. Pyramidal starting geometries also lead to planar optimized structures. The NCS· radical presents an interesting case of symmetry breaking by giving true minima (absence of virtual frequencies) for the linear C_{infh} *and* the bent C_s geometry. The bent structure is lower in energy by 0.5 kcal at the CBS-Q and G3 level. The structure of the CH_3S· radical deviates from the expected C_{3v} symmetry. Consistent with a hyperconjugative stabilization, one of the three C–H bonds is elongated and the respective H–C–S angle compressed.

Conclusions

A number of experimental sulfur–sulfur bond energies found in the literature show large discrepancies (> 10 kcal) and strong deviations from high-precision values obtained through CBS-Q and G3 calculations (this study).

1. For difluorodisulfane, FSSF, the high-precision value of 77.7 kcal differs significantly form the two conflicting literature values of 61.0 ± 4.0 kcal (Benson)[17] and 86.6 kcal (NIST database)[58] but is in excellent agreement with the value of 77 kcal reported by Lösking, Willner et al.[57]

2. The experimental sulfur–sulfur bond energy of disulfane, HSSH, has been reported as 66.0 ± 2 kcal,[17] slightly higher than the high-precision value of 62.0 kcal in this study.

3. For MeSSMe, the high-precision value of 63.9 kcal is significantly lower than the literature value of 72.4 ± 1.5 kcal mol^{-1}[18b] but in very good agreement with the value of 65.2 ± 0.9 kcal obtained by Nicovich et al.[18a]

4. Judging by the high-precision value of 46 kcal for the sulfur–sulfur bond energy in thiocyanogen, NCS–SCN, homolytic dissociation into radicals is an unlikely pathway for the room-temperature decomposition of thiocyanogen ("dirhodan") to *para*-thiocyanogen, $(SCN)_n$.

5. For S_8, the G3 and CBS-Q data give a bond energy of 40.5 kcal, which is higher than the value tentatively suggested by Benson (32.5 kcal).[17] As the Hartree-Fock structures underlying the CBS-Q and G3 calculations do not reflect the weak stabilizing 1,4-nonbonding interaction present in the S_8 diradical, the true bond energy of S_8 may be slightly lower. The inclusion of CBS-QB3 data[62] and the consideration of the maximum absolute errors documented for the G3, CBS-Q, and CBS-QB3 methods[28] allows refined predictions for the ring opening of S_8: 37.2–38.4 kcal (ΔE_o), 38.0–39.2 kcal ($\Delta E°$), 38.0–39.2 kcal ($\Delta H°$), and 32.5–33.4 kcal ($\Delta G°$) [38.0–39.2 kcal for $\Delta H°$].[62]

6. The use of the recently (2005) introduced BMK method, which has been specifically optimized for thermochemical calculations instead of the frequently used B3LYP method leads to significantly improved bond energies. For the sulfur–sulfur bond energy, the average error is reduced from 7.07 kcal (B3LYP) to 1.91 kcal mol^{-1} (BMK), approximately 6 kcal mol^{-1} in absolute terms and more than threefold in relative terms.

7. The DFT structures of disulfanes XSSX are not fully converged at the DFT/6-311G(2d,p) level. Excellent computational structures are obtained with the MPW1PW91 and B1B95 hybrid DFT methods and the 6-311G(3df,p) basis set. Other DFT methods used in this study gave sulfur–sulfur bond lengths that were either too long (B3LYP, BMK, B98) or too short (BB1K, MPWB1K, MPW1B95).

Supporting Information (see footnote on the first page of this article): A list of electronic energies (in Hartrees) obtained in the CBS-Q, G3, and DFT calculations.

Acknowledgments

We thank Prof. Gordon Lange for valuable comments relating to the present work.

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[61] B. Giese, *Radials in Organic Synthesis*, Pergamon, **1986**.

[62] Note added in proof: The CBS-QB3 method,[28] which reproduces the 1,4 interaction via its B3LYP/CBS7 structure does indeed lead to a slightly lower bond energy for S_8: 36.5 (ΔE_o), 37.3 ($\Delta E°$), 37.3 ($\Delta H°$) and 31.5 ($\Delta G°$) kcal. With the maximum errors of the three methods for bond energies,[28] we obtain the following bond energies for S_8 ($\Delta H°$): 37.3 ± 1.9 kcal (CBS-QB3), 40.3 ± 2.3 kcal (CBS-Q), and 40.8 ± 4 kcal (G3). The CBS-Q data define a lowest limit of 38.0 kcal, the CBS-QB3 data a highest limit of 39.2 kcal. This allows a prediction of 38.0–39.2 kcal for the bond energy ($\Delta H°$) in S_8. The other energies for S_8 can similarly be narrowed to 37.2–38.4 kcal (ΔE_o), 38.0–39.2 kcal ($\Delta E°$), and 32.5–33.4 kcal ($\Delta G°$). For the disulfanes (X: H, F, Cl, OH, and NH_2) and tetrasulfane, HSS–SSH, the CBS-QB3 energies are identical to the G3 and CBS-Q data within the maximum error margin of the CBS-QB3 method (1.9 kcal).

Received: September 2, 2008
Published Online: February 26, 2009

