

Search for a *trans*-Disulfide: Structural Analysis of Di-*tert*-adamantyl Disulfide by Photoelectron Spectroscopy, Derivation of $\sigma_I(t\text{-Ad})$, and Molecular Mechanics Calculations for Related Bulky Disulfides¹

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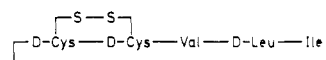
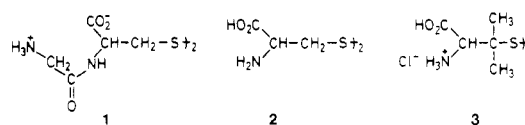
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Photoelectron spectroscopy of *t*-Ad-SS-*t*-Ad yields an $IE(n_s) - IE(n_a)$ energy difference of 0.51 eV at the frontier orbital gap suggesting to an S-S dihedral angle of $\theta(\text{CSSC}) = 103^\circ$. Molecular mechanics calculations with Allinger's MMI yield a shallow energy minimum with respect to rotation about the S-S bond. Two conformations differing by 0.7 kcal/mol are located at $\theta(\text{CSSC}) = 100$ and 114° . Regression analysis of dialkyl disulfide ionization energies and substituent inductive parameters (σ_I) leads to $\sigma_I(t\text{-Ad}) = -0.089$, indicating *t*-Ad to be a better electron donor than *t*-Bu. Finally force field calculations for several sterically congested disulfides suggest that *trans* disulfides may be realizable for very large alkyl substituents such as the $(t\text{-Bu})_3\text{C}$, polymethyladamantyl, and trimethylperhydrotriquinicyl moieties.

Disulfides comprise a class of sulfur compounds with a unique and rich chemistry.² The ease with which the S-S bond is formed and broken is no doubt reflected in the fact that disulfides unassociated with proteins are found widely distributed in nature.³ The adjacency of two lone pair bearing sulfur atoms provides the additional fascination that a stereoelectronic effect arises from the interaction of the nonbonding electrons. The resulting energy distribution as a function of the CS-SC dihedral angle has received considerable attention recently by means of Raman,^{4,5} UV,⁶⁻⁹ and photoelectron spectroscopy.⁹⁻¹² Apart from their intrinsic value, the conformational features of disulfides are of interest in connection with the secondary structure of proteins.^{4,5} Several groups have, for example, attempted to correlate S-S stretching frequencies with $\theta(\text{CSSC})$ and $\theta(\text{CCSS})$ in relatively simple model disulfides in the hope that the findings might be extrapolated to the more complicated cystine-containing systems including

proteins.^{4,5} This effort has met with limited success for a number of reasons, one of which is the lack of adequate model substances with $\theta(\text{CSSC}) \geq 100^\circ$.^{4b}

The "natural" S-S dihedral angle for strain-free disulfides is well established as $80-85^\circ$. Placement of the disulfide moiety in a ring can cause reductions of $\theta(\text{CSSC})$ to nearly 0° .^{4b,6,8,13} Remarkably few torsional angles larger than 85° have been observed. A trio of notable exceptions in the solid state are *N,N'*-diglycyl-L-cystine dihydrate (1),¹⁴ L-cystine (2)¹⁵ (hexagonal), and D-penicillamine disulfide (3),¹⁶ with $\theta(\text{CSSC}) = 101, 106$, and 115° , respectively, as determined by X-ray analysis.¹⁷



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The angle expansion for **3** with a tertiary carbon α to sulfur is not unexpected and is comparable to that found for di-*tert*-butyl disulfide ($\theta(\text{CSSC}) \sim 110^\circ$) based on PES measurements.^{10,11} However the cystine derivatives **1** and **2** in which a primary carbon is α to sulfur possess S-S torsional angles $15-20^\circ$ larger than those of the hydrocarbon analogue. The torsional distortion is probably related to the geometrical requirements arising from the extensive intermolecular hydrogen bonding observed in the crystalline state. Furthermore cystine **1** shows an abnormally short intermolecular S...CH₂ distance, presumably due to packing effects.¹⁴ The S-S dihedral angle opening may imply a synergic relaxation.

An unusually large S-S twist angle of $130-140^\circ$ was proposed for malformin A (**4**) on the basis of CD and NMR evidence.¹⁸ Subsequent structure revision¹⁹ has caused

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(18) M. Ptak, *Biopolymers*, **12**, 1575 (1973).

Table I. Experimental Vertical Ionization Potentials of Some Adamantane Derivatives^a

		σ_1	σ_2	σ_3	σ_4	ref
di- <i>tert</i> -adamantyl disulfide, DAD	7.86 (n.), 8.37 (n.)	9.8	11.4	13.5	14.9	this work
1-adamantanethiol	8.78 (n _S)	9.87	11.6	13.5	15.2	this work
adamantane		9.75	11.25	13.40	15.10	25a

^a The vertical IP's are taken as the maxima of the Frank-Condon envelopes (eV).

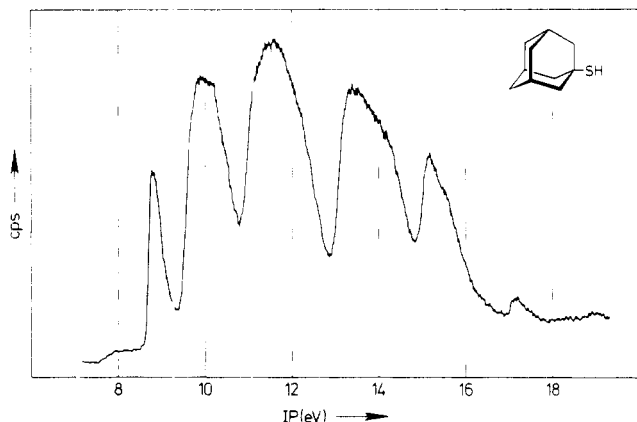
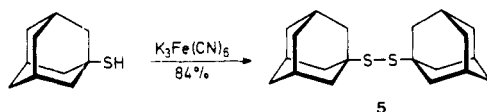


Figure 1. Photoelectron spectrum of 1-adamantanethiol.

a concomitant angle revision downward to 35°. Similar spectroscopic measurements in connection with molecular model considerations have led to suggestions that 20-membered peptide rings containing a disulfide fragment possess $\theta(\text{CSSC}) \sim 120^\circ$.²⁰ Finally cystine residues in a number of proteins have been reported as sustaining S-S torsions of 100–130°. Two exceptional cases were cited as showing $\theta(\text{CSSC})$ at ca. 145 and 165°.²¹

The paucity of simple disulfides with $\theta(\text{CSSC}) \geq 100^\circ$ motivated us to examine the relatively bulky diadamantyl disulfide (5) (DAD) and to estimate its dihedral angle



spectroscopically. The experimental work has been supplemented by force field calculations on this and even bulkier systems with the goal of identifying promising target structures with potential for a trans S-S geometry.

Synthesis of Di-*tert*-adamantyl Disulfide (DAD). The preparation of DAD (5) is unexceptional and accomplished in 84% yield by oxidizing 1-adamantanethiol²² with potassium hexacyanoferrate. DAD has been prepared previously by employing slightly different oxidation procedures.²³ The earlier reports, however, provide little information regarding its physical properties and associated structural characteristics. The structure of DAD is supported by elemental analysis and by molecular weight determination via field ionization mass spectrometry (M^+ , m/e 334). The S-S stretching frequency appears in the Raman spectrum of the solid at 542 cm^{-1} in accord with

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Table II. Alkyl σ_1 Constants and PES-Determined IE's (eV) for Thiols (RSH) and Disulfides (RSSR)

R	$-\sigma_1^a$	IE ₁ ^b (RSH) ^b	RSSR			
			Bock/Wagner ^c		Guimon et al. ^d	
			IE ₁	(IE ₁ + IE ₂)/2	IE ₁	(IE ₁ + IE ₂)/2
H	0.0	10.47 ^e	10.01	10.15		
CH ₃	0.046	9.44	8.97	9.09	9.00	9.13
Et	0.057	9.29	8.70	8.81	8.77	8.89
<i>n</i> -Pr	0.061	9.19	8.62	8.75		
<i>n</i> -Bu	0.063	9.15			8.51	8.62
<i>i</i> -Pr	0.065	9.14	8.54	8.65	8.51	8.63
<i>t</i> -Bu	0.074	9.03	8.17	8.50	8.15	8.45
<i>t</i> -Ad	0.089 ^f	8.78 ^f	7.86 ^f	8.12 ^f	7.86 ^f	8.12 ^f

^a Taken from ref 31, Table 11. ^b Reference 27. ^c Reference 10. ^d Reference 11. ^e A. W. Potts and W. C. Price, *Proc. R. Soc. London*, **326**, 181 (1972). ^f This work.

Table III. Least-Squares Correlation Lines, IE = $a_1 \sigma_1 + c$, for the Dependence of PES-Determined IE's on σ_1 ; Calculated σ_1 (*t*-Ad)

PES series	a_1 , eV	c	r	$-\sigma_1$ (<i>t</i> -Ad)
RSH: Ogata et al. ^a	20.14	10.44	0.994	0.083
Levitt ^b	22.2	10.46	0.999	0.086
RSSR: Bock/Wagner ^c				
IE ₁	12.60	10.12	0.998	0.090
(IE ₁ + IE ₂)/2	11.38	10.14	0.999	0.089
Guimon et al. ^d				
IE ₁	12.21	10.07	0.994	0.090
(IE ₁ + IE ₂)/2	11.72	10.17	0.997	0.088
Levitt, ^e IE ₁	10.70	13.55	0.998	0.086

^a Column 3, Table II. ^b Reference 29. ^c Columns 4 and 5, Table II. ^d Columns 6 and 7, Table II.

^e Reference 42.

tertiary carbon attachment to sulfur.^{4,5,24} Two low-energy ionizations at 7.86 and 8.37 eV in the PE spectrum are characteristic of the dialkyl disulfide fragment.⁹⁻¹² Finally the ¹H and ¹³C NMR spectra reveal the presence of the adamantyl moiety.

Photoelectron Spectrum of 1-Adamantanethiol. The PE spectrum of 1-adamantanethiol (Figure 1) contains a single sharp band at 8.78 eV and four distinctive ionizations from 9 to 16 eV. The latter are qualitatively superimposable with those found for adamantane and other 1-substituted adamantanes and are clearly associated with the adamantane σ -bond framework²⁵ (cf. Table I). The shape and position of the first IE leave little doubt that it corresponds to a sulfur lone electron pair ionization. Previously recorded alkanethiol PE spectra display the

(24) Bis(2-adamantyl) disulfide is known: J. W. Greidanus, *Can. J. Chem.*, **48**, 3530 (1970); J. R. Bolton, K. S. Chen, A. H. Laurence, and P. de Mayo, *J. Am. Chem. Soc.*, **97**, 1832 (1975); P. de Mayo, *Acc. Chem. Res.*, **9**, 58 (1976).

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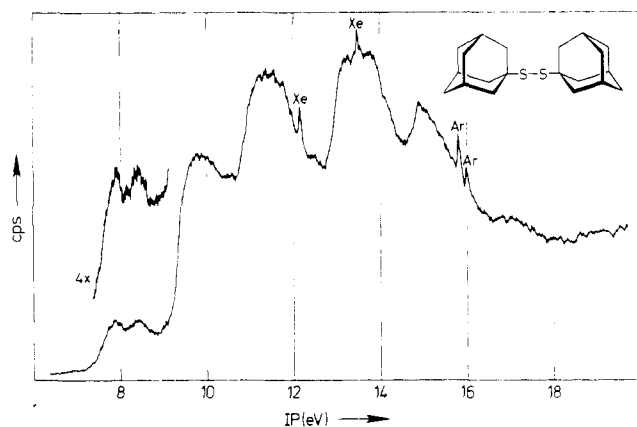


Figure 2. Photoelectron spectrum of di-*tert*-adamantyl disulfide (DAD).

first lone pair peak from 9.5 to 9.0 eV.^{10,26-28} The variation with substitution shows that the stepwise addition of alkyl groups serves to raise the energy of the high-lying n_S (π) in a regular manner (Table II). The increment of 0.25 eV from *t*-Bu to *t*-Ad is entirely consistent with the 0.11–0.15-eV destabilization found for the lower alkyl homologues.

Energy lowering of the sulfur nonbonding electrons in both thiols and disulfides has been attributed to closed-shell repulsion arising from the mixing of the low-lying MO's of the alkyl fragment with the sulfur n_S (π) orbital^{10,27} and to the donor inductive effect of alkyl groups.^{10,26,29,30} A quantitative measure of the latter has been derived by a least-squares plot of thiol photoionization IE's vs. the inductive substituent constant, σ_I .^{29,30} The resulting correlation line (cf. Table III) is thus, in principle, capable of yielding a σ_I value for the bridgehead substituted adamantyl moiety.³² Although σ_p , σ_p^+ , and σ_R^0 constants have been reported for the adamantan-1-yl group,³⁷ to our knowledge a reliable σ_I is not available.³⁸ Since photoionization data correspond to adiabatic ionization potentials,³¹ we take the onset of the band in Figure 1 (8.55 eV) to calculate $\sigma_I(t\text{-Ad}) = -0.086$. We return to this point below.

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(32) The development of σ_I parameters is not without complications or controversy. It has been argued that σ_I , in addition to containing an inductive contribution, likewise includes polarizability,^{31,33,34} steric,³⁵ and resonance components.³⁵ In addition, Charton's recently defined σ_I leads to values of -0.01 ± 0.01 for all alkyl and cycloalkyl groups, the differences being insignificant.^{35a,36} Our value of $\sigma_I(t\text{-Ad})$ is meant to be utilized within the Taft-Levitt framework^{31,34} and clearly reflects a composite of various effects.

(33) R. W. Taft, M. Taagepera, J. L. M. Abboud, J. F. Wolf, D. J. DeFrees, W. J. Hehre, J. E. Bartmess, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **100**, 7765 (1978).

(34) R. W. Taft and L. S. Levitt, *J. Org. Chem.*, **42**, 916 (1977).

(35) (a) M. Charton, Correlation Analysis Conference, Assisi, 1979; (b) M. Charton, private communication.

(36) M. Charton, *Prog. Phys. Org. Chem.*, in press.

(37) T. J. Broxton, G. Capper, L. W. Deady, A. Lenko, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 1238 (1972).

(38) An estimate of $\sigma^*(t\text{-Ad}) = -0.26$ from ³⁵Cl nuclear quadrupole resonance measurements³⁹ is convertible into the inductive constant by means of the equation $\sigma_I = -0.046(1 - 2\sigma^*)$ ³¹ and gives $\sigma_I = -0.070$, clearly an underestimate.

(39) M. G. Voronkov, V. P. Feshin, and J. Polis, *Teor. Eksp. Khim.*, **7**, 555 (1971); *Chem. Abstr.*, **76**, 33456a (1972).

Photoelectron Spectrum of *t*-Ad-SS-*t*-Ad; $\sigma_I(t\text{-Ad})$.

The trace in Figure 2 illustrates that DAD yields, in addition to the characteristic adamantane ionizations (Table I), two relatively low-energy IE's at 7.86 and 8.37 eV. There is ample precedent for assigning these to the antibonding (n_-) and bonding (n_+) combinations of the $p-\pi$ type lone pairs on sulfur.⁶⁻¹² Furthermore, a body of experimental and theoretical data have led to a correlation between the difference $IE(n_-) - IE(n_+)$ and $\theta(\text{CSSC})$.⁹⁻¹¹ For S-S torsional angles below 90° there are complementary structural (X-ray, ED, and MW) and PES data.^{9,11} However for $\theta(\text{CSSC}) > 90^\circ$, the single available angle has been "guestimated" for *t*-Bu-SS-*t*-Bu ($\sim 110^\circ$) by a combination of extended Hückel calculations and PES measurements.^{10,11,40} On this basis, the lone pair split for DAD, $\Delta IE = 0.51$ eV, implies a value for the S-S torsion of either 73 or 103° .¹¹ The lower angle can be excluded since $\theta(\text{CSSC})$'s below 80° are observed only when the S-S moiety is present as part of a small or rigid ring. The larger value is then subject to the uncertainty of the $\Delta E/\theta$ correlation extrapolated beyond 90° .

Thus we conclude that $\theta(\text{CSSC})$ for di-*tert*-adamantyl disulfide is of the order of 20° larger than the natural disulfide angle, but far short of the 180° trans value. In the next section we consider an unknown series of simple dialkyl disulfides which may well possess the desired S-S torsional expansion.

First, however, we return to a consideration of the relative IE's of thiols and disulfides as a function of alkyl substituent. As mentioned above Levitt and Levitt have derived correlations for the relationship of first ionization potentials and σ_I .^{29,30,42} However the data employed originates from photoionization, electron impact, and PES measurements and is therefore not entirely consistent with the present IE values. Furthermore the disulfide correlation⁴² utilizes only first ionization potentials. The latter are influenced both by substitution and by the value of the S-S dihedral angle. Thus, while the n_-/n_+ or IE_1/IE_2 split reflects the magnitude of $\theta(\text{CSSC})$, the average $[(IE_1 - IE_2)/2]$ can be taken as a measure of substitution effects in the absence of a conformational influence. The relevant PES quantities are given in Table II. As the accuracy of PES ionization energies is traceable, in part, to the reference standards employed, the Bock/Wagner and Guimon et al. measurements are treated separately.⁴³ The resulting least-squares regression lines are found in Table III.

The various correlations, as measured by the correlation coefficient, r , are good to excellent and agree in placing $\sigma_I(t\text{-Ad})$ from -0.08 to -0.09 . The RSH (Ogata) and RSSR (Levitt) series contain IE determinations from different sources, which may account for the relatively low σ_I 's derived. The average value from the remaining internally consistent disulfide regression lines is $\sigma_I(t\text{-Ad}) = -0.089$. This number is to be compared with the quantities -0.0896 and -0.0897 calculated by employing the "delocalization" and "through the bond" models of alkyl induction.³¹ As a consequence we take it to be the "best" $\sigma_I(t\text{-Ad})$ and have included it in the Table II tabulation.³² The *t*-Ad fragment is clearly implied to be a better electron donor than *t*-Bu. Independent experiment is corroborative.^{37,44}

(40) The *tert*-butyl disulfide S-S angle has also been assigned values of 96° and 98° ;^{12a} cf., however, ref 9 (ref 33 therein).

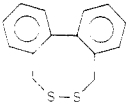
(41) B. Nelander, *Acta Chem. Scand.*, **23**, 2127 (1969).

(42) L. S. Levitt and B. W. Levitt, *Chem. Ind. (London)*, 132 (1973).

(43) Bock and Wagner used argon gas as reference,¹⁰ whereas Guimon and co-workers employed a mixture of argon and xenon.¹¹

(44) I. Mazeika, I. S. Yankovskaya, and J. Polis, *Zh. Obshch. Khim.*, **41**, 1633 (1971); *Chem. Abstr.*, **75**, 140113n (1971).

Table IV. Selected Features of the Molecular Mechanics (MMI) Structure of DAD Compared to Other Disulfides (Bond Lengths, Å; Angles, deg)

	DAD		<i>t</i> -Bu-SS- <i>t</i> -Bu	CH ₃ -SS-CH ₃			
	calcd ^a	exptl ^b	calcd ^c	exptl ^d (ED/MW)	calcd ^e	exptl ^e	calcd ^f
<i>r</i> SS	2.029	2.049	2.029	2.022/2.038	2.030	2.035	2.027
<i>r</i> SC	1.845	1.866	1.847	1.806/1.810	1.818	1.835	1.820
<i>r</i> CC	1.535	1.511-1.571	1.533-1.540				
∠SSC	106.2	105.5	106.2	104.1/102.8	103.7	104.3	103.4
∠SCC	110.0	103.1-113.8	106.4-110.5				
θ(CSSC)	113.8	115	113.8	83.9/84.7	83.2	56.4	64.1

^a This work. ^b Reference 16. ^c MMI, ref 1. ^d ED: B. Beagley and K. T. McAloon, *Trans. Faraday Soc.*, **67**, 3216 (1971); MW: D. Sutter, H. Dreizler, and H. D. Rudolph, *Z. Naturforsch.*, **A**, **20**, 1676 (1965). ^e G. H. Wahl, Jr., J. Bordner, D. N. Harpp, and J. G. Gleason, *J. Chem. Soc., Chem. Commun.*, 985 (1972). ^f MMI, ref 46.

Molecular Mechanics Evaluation of Very Bulky Disulfides.

The preparation of trans disulfides is of inherent interest since the antiperiplanar stereochemistry represents a simple but unknown geometric extreme for the S-S unit. From a more practical viewpoint, the absence of trans or near-trans disulfides often forces the researcher to depend exclusively on extrapolations of uncertain validity and on the results of theoretical calculations for S-S dihedral angle determination. As described above, the estimate of θ(CSSC) for DAD is based on a semiempirical PES correlation for which only indirect structural evidence obtains for S-S torsional angles above 91°.⁹⁻¹¹ Calculations of the electronic absorption spectra of disulfides have resulted in another correlation, the position of the first absorption band in the UV and θ(CSSC).^{6,7,9} The calculations, however, are unable to reproduce the UV spectrum of *t*-Bu-SS-*t*-Bu with an enhanced CS-SC angle of ca. 110°.⁴⁵ A third attempt to provide θ(CSSC) estimates has utilized CNDO/2 calculated S-S stretching frequencies as the correlate.¹³ Experimental trends can be reproduced from 0 to 80°, but it was remarked that the lack of suitable model compounds prevents any realistic appraisal of larger angles.^{4b}

Although disulfides with θ(CSSC)'s less than 85° can be prepared by the expediency of ring formation, this strategy is of little value for small molecular weight trans systems. The low polarity of the disulfide likewise prevents the potential exploitation of medium effects as a mediator of conformation. Steric repulsion has been suggested as a possible means of achieving θ(CSSC) enlargement. Our recent force field study of alkyl disulfides with Allinger's MMI program, for example, demonstrated that increasing substituent size tends to drive the RSSR conformation in the direction of the trans barrier.¹ The low energy conformation of the bulkiest system investigated, *t*-Bu-SS-*t*-Bu, was predicted to have θ(CSSC) = 114°, in excellent agreement with the PES/MO estimate. We have extended these studies, using the same computational tool, to DAD and to even bulkier disulfides.

The calculations for DAD were performed by fixing the S-S dihedral angle at 20° increments from 0 to 180° and completely optimizing all other bond lengths and angles with the Allinger force field.⁴⁶ Heats of formation and the attendant strain energies were obtained with our supplemental parameters.¹ The resulting hypersurface is

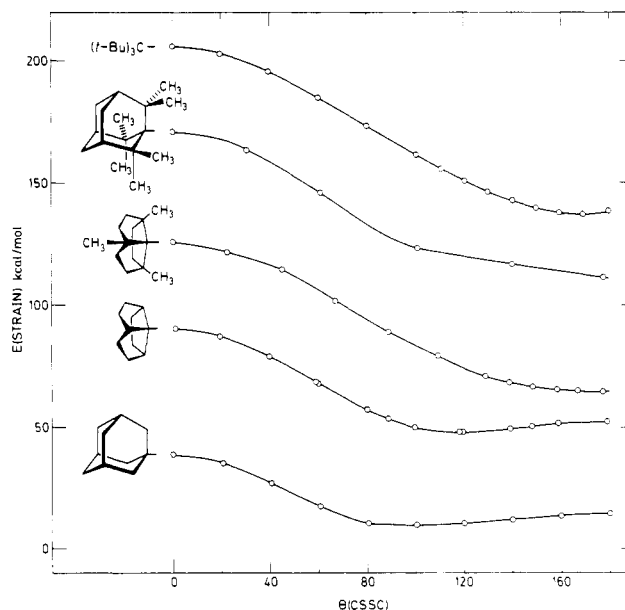


Figure 3. The CS-SC dihedral angle-strain energy dependence for a series of bulky acyclic symmetrical disulfides. At each point, θ(CSSC) was fixed at the indicated value, and the remainder of each molecular structure was fully geometry-energy optimized by the MMI force field method.

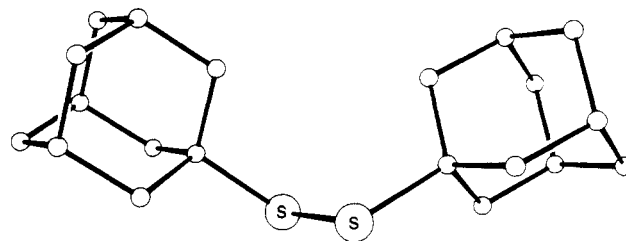


Figure 4. ORTEP drawing of the minimum energy conformation of *t*-Ad-SS-*t*-Ad (DAD, θ(CSSC) = 114°) as determined by force field calculations (MMI).⁵⁸

shown in Figure 3. The potential minimum is quite shallow, the trans and the cis barriers amounting to 5.3 and 29.7 kcal/mol, respectively, analogous to the previous calculations. Unrestricted optimization of DAD yields the structure pictured in Figure 4 with an S-S dihedral angle of 113.8°. Both adamantyl residues adopt staggered conformations as illustrated with Newman projections in Figure 5a. The remaining structural parameters are unexceptional and tallied in part with experimental comparisons in Table IV. Rotation of one of the adamantyl moieties into an eclipsed relationship followed by reop-

(45) CNDO-CI calculations on the optical rotary properties of the chiral disulfide chromophore are, however, able to predict the sign of CD bands.^{7,8a} The results are supportive of the speculative θ(CSSC) = 120° for (2,7-cystine)gramicidin S.²⁰

(46) N. L. Allinger, M. J. Hickey, and J. Kao, *J. Am. Chem. Soc.*, **98**, 2741 (1976).

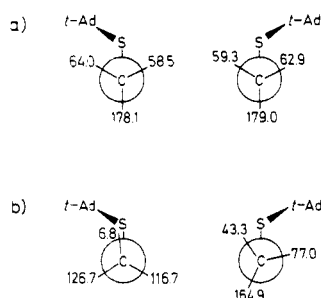
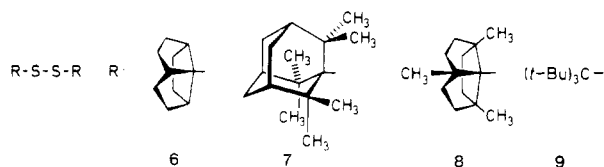


Figure 5. Newman projections of the two minimum energy conformations of *t*-Ad-SS-*t*-Ad (DAD). The numerical values indicate the CC-SS dihedral angles for the adamantyl group projecting in the direction of the reader. The right-left relationship pictures the individual adamantyl moieties within the same conformation: (a) the fully staggered rotamer; $\theta(\text{CSSC}) = 114^\circ$, $E_{\text{strain}} = 9.0$ kcal/mol; (b) the partly eclipsed conformation; $\theta(\text{CSSC}) = 100^\circ$, $E_{\text{strain}} = 9.7$ kcal/mol.

timization leads to the conformer shown in Figure 5b. The CS-SC dihedral angle has dropped to 100.2° with an increase in total energy of 0.7 kcal/mol. The existence of eclipsed forms residing in potential energy minima has been described earlier¹ and appears to be a general consequence of the "cogwheel" interaction in bulky disulfides. One of its attributes is the energetically inexpensive population of conformers with substantially different $\theta(\text{CSSC})$'s. The flat minimum for DAD (Figure 3) is partly associated with this phenomenon. For the sake of qualitative evaluation, if we convert the calculated 0.7 kcal/mol mentioned above into an equilibrium constant, only 70–80% of the more stable conformer is expected. The $\Delta E(n_- - n_+)$ obtained from the PE spectrum may, therefore, reflect a weighted average due to a conformer mix. The deviation of $\theta_{\text{calcd}}(\text{CSSC}) = 113.8^\circ$ from $\theta_{\text{PES}}(\text{CSSC}) = 103^\circ$ can be ascribed to the same source, as well as to uncertainties in the *t*-Bu-SS-*t*-Bu angle used as the basis for the PES estimate.

Similar molecular mechanics calculations were carried out for diperhydrotriquinacene disulfide (6). The pre-



dicted $\theta(\text{CSSC}) = 119.5^\circ$ (Table V), the two-dimensional energy surface resembling that of DAD (cf. Figure 3). Although the individual hydrocarbon moieties are superimposable, they are calculated to be twisted and chiral, as recently described by Osawa for the parent perhydrotriquinacene.^{47,48} Polymethylation of DAD and perhydrotriquinacene 6 to give the structures 7 and 8 yields the desired result. The conformational energy surface with respect to the S-S bond contains only a single maximum at $\theta(\text{CSSC}) = 0^\circ$ connected to the trans minimum by a continuous downhill slope. The tri-*tert*-butylmethyl disulfide 9 is a third example. Within the Allinger molecular mechanics scheme, steric bulk of the magnitude represented by structures 6–9 appears to be sufficient to achieve the antiperiplanar geometry. Any number of substitution

Table V. Disulfide S-S Dihedral Angles, Heats of Formation, Strain Energies, and Relative Conformational Energies for Selected Bulky Disulfides

R	$\theta(\text{CSSC})$, deg	ΔH_f° , ^a kcal/mol	strain, ^a kcal/mol	E_{rel} , kcal/mol
	0.1 max		38.68	29.71
	113.8 min	-50.0	8.97	0.00
	179.9 max		14.24	5.27
	1.0 max		89.96	41.98
	119.5 min	-11.0	47.98	0.00
	178.9 max		52.43	4.45
	0.0 max		125.95	60.98
	177.7 min	-47.2	64.97	0.00
	0.2 max		171.10	59.67
	177.5 min	-40.2	111.43	0.00
	0.0 max		206.29	68.58
	168.9 min	-40.1	137.71	0.00
	179.6 max		138.78	1.07

^a Calculated by means of the parameters derived in ref 1.

patterns should have comparable stereochemical consequences and serve equally well as targets for simple trans disulfide models.^{49,50}

It is worth adding a reservation to the numerical results for large angle distortions given in Table V. Force field parameterization depends exclusively on the availability of empirical data. Evaluation of molecular structures and energies is at its best when the system in question resembles those used in the parameterization. Disulfide geometric parameters are based on the structure of *gauche* dimethyl disulfide and have been shown to adequately treat monocycles with $\theta(\text{CSSC}) < 85^\circ$.⁴⁶ The ΔH_f° parameters, on the other hand, include both acyclic unstrained and moderately strained species.¹ The complete absence of gas-phase or crystal structures for uncomplicated dialkyl disulfides with S-S torsions $> 85^\circ$ (cf. Table IV) reduces the reliance that can be placed on the detailed accuracy of the trans geometries predicted for 6–9. The influence of steric repulsion can nonetheless be inferred experimentally from the torsions about the analogous CO-OC bond found for peroxides *t*-Bu-OO-*t*-Bu,⁵¹ Me₃Si-OO-SiMe₃,⁵¹ and Ph₃C-OO-CPh₃⁵² ($\theta(\text{XOOX}) = 160, 178, \text{ and } 180^\circ$, respectively). Relative to the disulfides, interpretation of the peroxide O-O torsional angles must be tempered with the knowledge that bond lengths to oxygen are shorter than those to sulfur and natural peroxide dihedral angles appear to be larger than for disulfides

(49) For example, the recently derived steric substituent parameter Δ_f (ref 50a) might prove useful for selecting trans-directing disulfide substituents.

(50) (a) H.-D. Beckhaus, *Angew. Chem.*, **90**, 633 (1978); *Angew. Chem., Int. Ed. Engl.*, **17**, 593 (1978); (b) D. F. DeTar and C. J. Tenpas, *J. Am. Chem. Soc.*, **98**, 4567, 7903 (1976); J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickason, and H. C. Brown, *ibid.*, **96**, 1969 (1974); W. T. Wipke and P. Gund, *ibid.*, **98**, 8107 (1976), and references in these citations.

(51) D. Käss, H. Oberhammer, D. Brandes, and A. Blaschette, *J. Mol. Struct.*, **40**, 65 (1977).

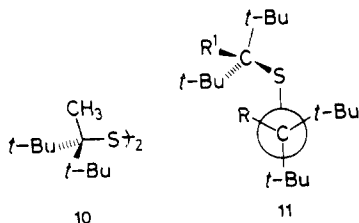
(52) C. Glidewell, D. C. Liles, and D. J. Walton, *Acta Crystallogr., Sect. B*, **35**, 500 (1979).

(47) E. Osawa, *J. Am. Chem. Soc.*, **101**, 5523 (1979).

(48) The S-S bond is calculated to lie above one of the three cyclopentane rings. Starting from a symmetrical perhydrotriquinacene fragment, the geometry optimization leads to $\theta(\text{CHCH}_2\text{-CH}_2\text{CH})$ values of 38.4, 30.8, and 19.4°. The last, smallest angle is that found in the five-ring facing the S-S bond. A detailed search of the hydrocarbon potential hypersurface for disulfide 6 has not been carried out.

($\theta(\text{HOOH}) = 110\text{--}120^\circ$;⁵³ $\theta(\text{HSSH}) = 90.5^\circ$).⁵⁴ Nevertheless, we anticipate that structures 6-9, if capable of preparation, will show large and "abnormal" $\theta(\text{CSSC})$'s at least approaching the trans values.

Attempts to synthesize highly congested disulfides may encounter unexpected problems. We should like to point out, however, that synthetically more attractive but sterically less crowded goals may ultimately prove disappointing. For example, $\alpha,\alpha,\alpha',\alpha'$ -tetra-*tert*-butyldiethyl disulfide (10) is a reasonably crowded system. However



it is likely to adopt 11 ($R = R' = \text{CH}_3$) as its minimum energy conformation. As we have pointed out previously, the value of $\theta(\text{CSSC})$ is determined by the substituents R and R' . Three sets of S-S dihedral angles were identified as follows: $83\text{--}84^\circ$ ($R = R' = \text{H}$), $94\text{--}96^\circ$ ($R = \text{H}$, $R' = \text{CH}_3$), $112\text{--}114^\circ$ ($R = R' = \text{CH}_3$).¹ On this basis it is predicted that 10 would resemble *t*-Bu-SS-*t*-Bu and DAD in its value of $\theta(\text{CSSC})$. Finally, the recent observation of a trans planar conformation in bis(2-pyrimidyl) disulfide acting as a ligand to Cu(I) should be mentioned.⁵⁵ Geometric distortion arises via the agency of nitrogen-copper complexation, however, as confirmed by X-ray⁵⁵ and force field calculations⁵⁶ for the free ligand.

Experimental Section

The PE spectra were recorded on a PS-18 spectrometer (Perkin-Elmer) and calibrated with a mixture of argon and xenon

(53) Experiment: R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *J. Chem. Phys.*, 1931 (1965); W. C. Oelfke and W. Gordy, *J. Chem. Phys.*, 51, 5336 (1969); theory: A. Veillard, *Theor. Chim. Acta*, 18, 21 (1970); T. H. Dunning and N. W. Winter, *Chem. Phys. Lett.*, 11, 194 (1971); *ibid.*, *J. Chem. Phys.*, 63, 1847 (1975); J. P. Ranck and H. Johansen, *Theor. Chim. Acta*, 24, 334 (1972).

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(55) C. J. Simmons, M. Lundeen, and K. Seff, *J. Chem. Soc., Chem. Commun.*, 595 (1979); *ibid.*, *Inorg. Chem.*, 18, 3444 (1979).

(56) D. B. Boyd and K. B. Lipkowitz, private communication.

gases introduced into the target chamber simultaneously with the sample. The recording temperatures for DAD and for 1-adamantanethiol were 97° and room temperature, respectively; the experimental resolution was 25-30 meV. The reported ionization potentials are averages of three determinations.

Bis(1-adamantyl) Disulfide. 1-Adamantanethiol⁵⁷ (4.4 g, 26 mmol) was slurried in a solution of sodium hydroxide (85% NaOH, 4.2 g, 85 mmol) in water (22 mL). A solution of potassium hexacyanoferrate(III) (8.7 g, 26 mmol) in water (42 mL) was added to the above-mentioned slurry during 3 h at room temperature. The reaction mixture was allowed to stand overnight. The reaction mixture was then extracted twice with ether. After the solution was dried with magnesium sulfate the ether was removed under reduced pressure, leaving the disulfide 5 as a white solid (3.7 g, 11 mmol, 84%). Recrystallization (pentane) gave 5 as colorless crystals, mp 223°C . Sublimation gave an analytical sample: ^1H NMR (CDCl_3 , Me_4Si) δ 1.68 (6 H, m), 1.85 (6 H, m), 1.93-2.04 (3 H, m); IR ν_{max} (KBr) 2900 (s), 2845 (s), 1450 (m), 1340 (m), 1310 (w), 1295 (m), 1255 (m), 1180 (w), 1100 (m), 1035 (m), 975 (m) cm^{-1} ; UV λ_{max} (CH_3CN) tailing to 280 nm; Raman ν_{max} (CCl_4) 532 cm^{-1} , ν_{max} (solid): 532, 542 cm^{-1} ; mass spectrum, m/e (relative intensity) 334 (M^+ , 8), 168 (2), 135 (100), 93 (7); ^{13}C NMR (CDCl_3 , Me_4Si) δ 30.1 (relative intensity 5.4), 36.2 (7.4), 43.2 (4.6), 47.3 (1.0). Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{S}_2$: C, 71.80; H, 9.04; S, 19.17. Found: C, 71.80; H, 9.29; S, 18.85.

Note Added in Proof. The X-ray structure determination of DAD has been completed and yields a value of $\theta(\text{CSSC}) = 110.5 (9)^\circ$,⁵⁹ in excellent agreement with the force field prediction of 113.8° . The PES estimate of the S-S torsion in DAD is obviously low, implying that the *t*-Bu-SS-*t*-Bu dihedral angle must be evaluated upward.⁵⁹

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Registry No. 5, 34895-45-9; 6, 72610-42-5; 7, 72638-41-6; 8, 72610-43-6; 9, 72610-44-7; 1-adamantanethiol, 34301-54-7.

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Mechanism of Formation of Grignard Reagents. Corrosion of Metallic Magnesium by Alkyl Halides in Ethers¹

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Scanning electron microscopy and optical microscopy have been used to examine the surface of magnesium that has been allowed to react with ether solutions of organic halides. Initiation of the reaction is characterized by the formation of isolated corrosion pits. These pits grow and eventually overlap, and a major part of the reaction takes place at a smooth, polished surface. The rate of reaction of polished magnesium with alkyl halides is relatively insensitive to the magnesium lattice plane exposed, to dislocation densities, and to grain boundaries. Initiation occurs rapidly at dislocations, relative to initiation at unstrained, intragranular magnesium surfaces.

This work examines the changes that accompany the reaction of metallographically prepared magnesium with

organic halides in diethyl ether.³ Its objective was to develop answers to two general questions that are funda-