filtered, and the solvent was evaporated, yielding 152 mg of crude product. Trituration with hexane afforded the methylated ketal (70 mg, 44%): mp 132–140 °C; NMR δ 1.15 (s, 3 H), 1.20 (s, 3 H), 1.25–2.0 (m, 5 H), 2.35 (d, 1 H, J = 16 Hz), 3.05 (s, 3 H), 3.9–4.05 (m, 4 H), 7.05 (s, 5 H), 7.2–7.6 (m, 5 H); IR 1670 cm^{-1}.

C. A solution of the methylated ketal (70 mg, 0.17 mmol), 6 N hydrochloric acid (1 mL), and ethanol (3 mL) was left at room temperature for 10 h. The solvent was evaporated, water was added to the residue (15 mL), and the product was extracted with methylene chloride (2 × 20 mL). The organic layer was then washed with water (3 × 15 mL), dried over anhydrous magnesium sulfate, and filtered, and the solvent was evaporated, yielding 56 mg of crude product which was recrystallized with isopropyl ether (left in freezer), affording 41 mg (67%) of pure **17**: mp 147.5–148 °C; NMR (CCl_4) 1.15 (s, 3 H), 1.20 (s, 3 H), 1.6–2.55 (m, 5 H), 2.80 (d, 1 H, J = 17 Hz), 2.85 (s, 3 H), 7.1 (s, 5 H), 7.25–7.6 (m, 5 H); IR 1720, 1640 cm^{-1}; mass spectrum (Finnigan 1015 S/L), *m/e* (relative intensity) 359 (2), 246 (10), 178 (100).

Anal. Calcd for $C_{24}H_{25}NO_2$: C, 80.19; H, 7.01; N, 3.90. Found: C, 80.08; H, 6.93; N, 4.01.

Registry No. 1, 886-38-4; **6a**, 1118-66-7; **6b**, 14092-14-9; **6c**, 7318-00-5; **6d**, 3389-57-9; **7a**, 75476-11-8; **7b**, 75476-12-9; **7c**, 75476-13-0; 8 (isomer 1), 75476-14-1; 8 (isomer 2), 75476-15-2; **10**, 75476-16-3; **11**, 75495-03-3; **13a**, 873-95-0; **13b**, 701-58-6; **13c**, 3357-16-2; **14**, 75495-04-4; **14**·ethylene ketal, 75476-21-0; **15** (isomer 1), 75476-17-4; **15** (isomer 2), 75476-23-2; **16a**, 75495-05-5; **16b**, 75476-18-5; **17**, 75476-19-6; **17**·ethylene ketal, 75476-22-1; **18**, 75476-20-9.

Crystal and Molecular Structure of Di-*tert*-adamantyl Disulfide. Extension of the Correlation between the Sulfur–Sulfur Dihedral Angle and the Sulfur Lone-Pair Energy Gap[1]

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The crystal and molecular structure of di-*tert*-adamantyl disulfide (1, DAD; $C_{20}H_{30}S_2$) has been determined from diffractometer data. The unit cell is monoclinic: space group $P2_1/c$; a = 12.015 (3), b = 11.556 (3), c = 12.959 (3) Å; β = 90.42 (2)°; V = 1799 Å^3; Z = 4; d_{calcd} = 1.24 Mg/m^{-3}. Least-squares refinements gave R = 0.074 for 649 observed reflections. The torsion angle θ(CSSC) = 110.5 (9)°. The observation of an enlarged S–S dihedral angle permits a tentative extension of the correlation between θ(CSSC) and the photoelectron spectroscopically determined ionization energy difference, $\Delta E(n_+ - n_-)$, and disulfide torsional angles above 90°. The molecular geometry of *t*-Bu–SS–*t*-Bu is revised accordingly.

Dialkyl disulfides represent a class of substances both intensely studied in the laboratory[2] and widely distributed in nature.[3] A singular structural feature of the disulfide moiety is its S–S dihedral angle of 80–85° in an unstrained molecular environment.[4] Deviations of up to 70° to smaller values of θ(CSSC) have been forced on the system by the expediency of ring formation. Although the unsubstituted parent, H_2S_2, enjoys an S–S torsional angle of 91°,[5] very few other examples with expanded θ(CSSC)'s are known. Notable exceptions are cysteine derivatives either strongly hydrogen bonded in the solid phase[6,7] or rigidly held in a protein.[8] Very recently a dipyrimidyl disulfide was found to sustain θ(CSSC) = 180° via the agency of copper complexation.[9]

Table I. Crystal Data for DAD

formula	$C_{20}H_{30}S_2$	V	1799.13 Å^3
fw	334.59	Z	4
space group	$P2_1/c$	temp	295 K
a	12.015 (3) Å	μ (Mo Kα)	0.62 mm^{-1}
b	11.556 (3) Å	d_{calcd}	Mg m^{-3}
c	12.959 (3) Å	cryst dimens	0.80 × 0.10 × 0.20 mm
β	90.4 (2)°		

Absent from the rich chemistry of the disulfide functionality is a series of simple derivatives with S–S dihedral angles spanning the 90–180° range. As part of a program designed to prepare and study these substrates, we have undertaken the X-ray structure determination of *t*-Ad–SS–*t*-Ad (DAD, 1). The results presented below confirm our molecular mechanics predictions of θ(CSSC) enlargement by means of bulky substituents[1b,10] and provide us with an opportunity to extend the θ(CSSC)/$\Delta E(n_+ - n_-)$ correlation beyond 90°.

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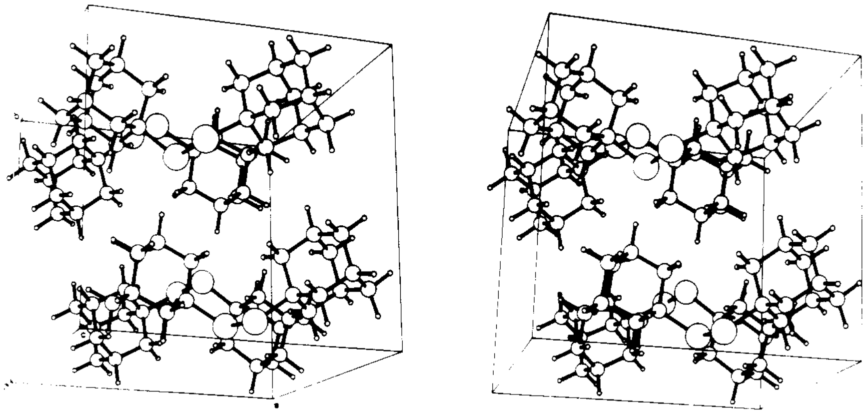

Figure 1. Stereoview of the packing of *t*-Ad-SS-*t*-Ad (1) (PLUTO).

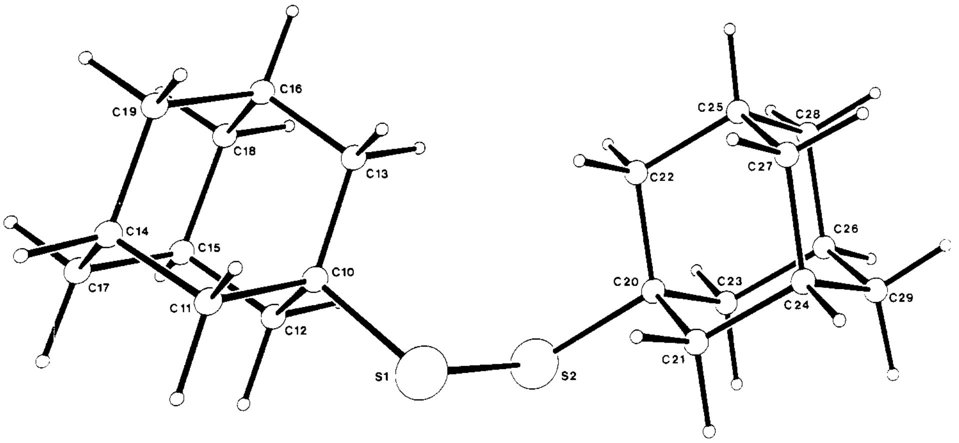

Figure 2. ORTEP representation of the three-dimensional X-ray structure of *t*-Ad-SS-*t*-Ad (1). The atom numbering corresponds to that given in Tables II-V.

Experimental Section

DAD (1) was prepared as described earlier.[1b] Suitable crystals were obtained by recrystallization from acetonitrile. The reflection intensities were measured with a four-circle diffractometer. Graphite-monochromatized Mo Kα radiation was used (λ = 0.710 73 Å). The crystal data are given in Table I. A total of 3511 unique reflections in the interval 0.07 < (sin θ)/λ < 0.62 Å^{-1} were obtained by the ω-scan technique. Only the 649 data having $I > 2\sigma(I)$ were corrected for L_p effects and used in the subsequent calculations.

The photoelectron spectra were recorded on a PS-18 spectrometer (Perkin-Elmer) and calibrated with a mixture of argon and xenon gases introduced into the target chamber simultaneously with the sample. The recording temperature for *t*-Bu-SS-*t*-Bu was room temperature and the experimental resolution was 35-40 meV. The reported lone-pair energy gap is the average of eight determinations.

Solution and Refinement

The structure was solved by direct methods and refined by full-matrix least-squares calculations. All observations were given unit weight, S atoms were refined with anisotropic thermal parameters, and C atoms were refined with individual isotropic thermal parameters. All H atoms were fixed in secondary CH_2 or tertiary CH groups with the C-H bond length taken as 1.08 Å. The maximum shift error for nonhydrogen atoms in the final least-squares refinement was 0.04, and R = 0.074. Final atomic coordinates and thermal parameters are given in Tables II and III. The packing of DAD is shown in Figure 1.

Table II. Fractional Atomic Coordinates ($\times 10^3$) and the Thermal Parameters ($\times 10^2$) for the Nonhydrogen Atoms[a]

	x	y	z	U, Å^2
S(1)	399 (0.4)	862 (0.5)	437 (0.4)	
S(2)	355 (0.4)	874 (0.5)	285 (0.4)	
C(10)	532 (1)	783 (2)	444 (1)	2.7 (5)
C(11)	568 (2)	796 (2)	559 (1)	5.0 (6)
C(12)	621 (2)	843 (2)	379 (2)	5.3 (6)
C(13)	524 (1)	657 (2)	417 (1)	3.7 (5)
C(14)	681 (2)	741 (2)	576 (2)	4.9 (6)
C(15)	734 (2)	787 (2)	394 (1)	3.8 (5)
C(16)	636 (1)	599 (2)	433 (1)	3.2 (5)
C(17)	766 (2)	797 (2)	507 (1)	5.3 (6)
C(18)	724 (2)	658 (2)	368 (1)	4.2 (5)
C(19)	673 (2)	612 (2)	549 (2)	5.7 (6)
C(20)	233 (2)	780 (2)	267 (2)	4.7 (6)
C(21)	143 (2)	811 (2)	345 (1)	4.3 (5)
C(22)	264 (2)	650 (2)	279 (2)	5.9 (6)
C(23)	192 (2)	801 (2)	157 (1)	3.7 (5)
C(24)	41 (2)	737 (2)	325 (2)	5.5 (6)
C(25)	162 (2)	574 (2)	259 (2)	5.7 (6)
C(26)	88 (2)	728 (2)	138 (2)	5.8 (7)
C(27)	70 (2)	607 (2)	335 (2)	5.4 (6)
C(28)	119 (2)	600 (2)	148 (2)	6.3 (6)
C(29)	−3 (2)	753 (2)	213 (1)	5.5 (6)

	U_{11}, Å^2	U_{22}, Å^2	U_{33}, Å^2	U_{23}, Å^2	U_{13}, Å^2	U_{12}, Å^2
S(1)	4.8 (4)	4.5 (4)	5.4 (4)	−1.7 (4)	−0.2 (3)	0.7 (3)
S(2)	5.0 (4)	4.0 (4)	6.3 (4)	2.3 (4)	2.3 (4)	−0.7 (3)

[a] Estimated standard deviations in parentheses. Carbon and sulfur atoms were refined with individual isotropic and anisotropic thermal parameters, respectively.

Atomic scattering factors were taken from the literature.[11] The structure analysis was performed with the SHELX system of programs;[12] illustrations were made with the PLUTO and ORTEP programs.[13]

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[11] "International Tables for X-ray Crystallography", Vol. 4, Kynoch Press, Birmingham, England, 1974.

Table III. Calculated Fractional Atomic Coordinates ($\times 10^3$) for H Atoms

	x	y	z
H(C11)1	509	753	607
H(C11)2	572	887	580
H(C12)1	627	933	401
H(C12)2	598	837	299
H(C13)1	463	617	466
H(C13)2	499	649	337
H(C14)	707	754	656
H(C15)	795	828	346
H(C16)	629	508	412
H(C17)1	773	888	527
H(C17)2	845	755	520
H(C18)1	803	616	381
H(C18)2	700	650	288
H(C19)1	753	572	561
H(C19)2	612	571	598
H(C21)1	174	794	422
H(C21)2	122	901	338
H(C22)1	329	629	225
H(C22)2	294	635	357
H(C23)1	171	891	148
H(C23)2	256	779	103
H(C24)	−21	762	380
H(C25)	184	484	267
H(C26)	59	747	61
H(C27)1	−4	556	320
H(C27)2	99	590	413
H(C28)1	182	577	94
H(C28)2	45	549	135
H(C29)1	−29	842	204
H(C29)2	−73	696	199

Table IV. Bond Lengths (Å)[a]

S(1)-S(2)	2.048 (7)	S(2)-C(20)	1.84 (2)
S(1)-C(10)	1.84 (2)	C(20)-C(21)	1.53 (2)
C(10)-C(11)	1.55 (2)	C(20)-C(22)	1.55 (3)
C(10)-C(12)	1.54 (2)	C(20)-C(23)	1.53 (3)
C(10)-C(13)	1.50 (2)	C(21)-C(24)	1.52 (3)
C(11)-C(14)	1.51 (2)	C(22)-C(25)	1.53 (2)
C(12)-C(15)	1.51 (2)	C(23)-C(26)	1.52 (2)
C(13)-C(16)	1.52 (2)	C(24)-C(27)	1.55 (3)
C(14)-C(17)	1.51 (3)	C(24)-C(29)	1.55 (2)
C(14)-C(19)	1.54 (3)	C(25)-C(27)	1.53 (2)
C(15)-C(17)	1.52 (2)	C(25)-C(28)	1.54 (3)
C(15)-C(18)	1.53 (2)	C(26)-C(28)	1.54 (3)
C(16)-C(18)	1.51 (2)	C(26)-C(29)	1.49 (3)
C(16)-C(19)	1.57 (3)		

[a] Estimated standard deviations in parentheses.

Results and Discussion

The molecule is shown in Figure 2 with the numbering of the atoms. The bond lengths are given in Table IV; the bond angles in Table V. The position of the molecule in the lattice is general in spite of the pseudo twofold rotation symmetry around the axis: $x = 0.387 - 0.0066T$, $y = 0.730 + 0.0861T$, $z = 0.355 + 0.0048T$. Within the adamantyl groups none of the bond lengths or bond angles are significantly different from those observed for other adamantanes.[14] The S-C bond lengths are found to be 1.84 Å, somewhat longer than the values for unstrained disulfides (for MeSSMe, 1.81,[15a,16] and 1.82 Å[15b]) but not as long as the S-C bonds in the cysteine derivative **2** (1.87 Å[7]). The S-S bond length is 2.048 Å, equal to that in **2** (2.049 Å[7]) but longer than the distance observed for MeSSMe (ED, 2.022[15a] and 2.029 Å[15b]; MW, 2.030 Å[16]). The S-S-C bond angles have been determined at 106.2° and 107.3°. These values are slightly increased relative to the angles in MeSSMe (ED, 104.1°[15a] and 103.2°;[15b] MW, 102.8°[16]) and **2** (105.5°[7]).

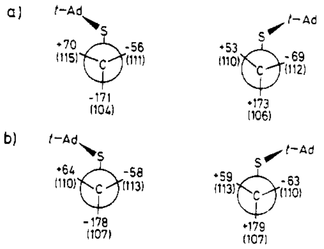
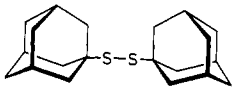


Figure 3. Newman projections of the conformation about the S-C bonds in *t*-Ad-SS-*t*-Ad (**1**). The numerical values indicate the torsional angles about the S(1)-C(10) and S(2)-C(20) bonds. The parenthetical quantities are the S(1)-C(10)-C and S(2)-C(20)-C bond angles. All values are in degrees: (a) X-ray determination (esd's for the torsional angles are 0.9°); (b) molecular mechanics.

Not unexpectedly, the S-C-C bond angles are dependent on the molecular environment. The conformational relationship of the adamantyl groups to the S-S bond in DAD is illustrated with Newman projections in Figure 3a. Consistent with a reduction in the nonbonded steric repulsion between the hydrocarbon fragments, the adamantyl moieties are twisted 5-10° from the perfectly staggered conformation. In harmony, the S-C-C bond angles with a trans relationship to the S-S-C unit (103.9° and 106.0°) are smaller than the bond angles exhibiting the corresponding gauche relationship (110-115°).

X-ray vs. Molecular Mechanics Structure. The molecular mechanics scheme used in our evaluations was originally parameterized by Allinger and co-workers[17a] for unstrained disulfides but has been shown to give correct structural values for strained disulfides with θ(CSSC) < 90°, that is, for disulfides in which the S-S moiety is part of a ring.[17] When employed for disulfides with θ(CSSC) > 90°, for example, DAD (**1**), the Allinger force field was likewise assumed to yield accurate structures.[1b] We are now able to compare the molecular mechanics structure of DAD with the X-ray determined geometry.

For the strained disulfides DAD (**1**),[1b] **2**,[7] and **3**[18] the force field underestimates by 0.01-0.02 Å the increase for the S-S and C-S bond lengths relative to lower dialkyl disulfide homologues.[15,16] Calculated and experimental S-S-C bond angles are, however, in excellent agreement, the differences being less than 1.0°. Variations between the calculated and experimental S-C-C bond angles in DAD amount to 2-3°.



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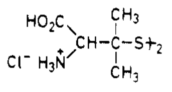

$$\left[Cl^- H_3\overset{+}{N}(HO_2C)CH{-}\underset{CH_3}{\overset{CH_3}{C}}{-}S{-}\right]_2$$

2

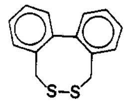

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Table V. Bond Angles (deg)[a]

C(10)-S(1)-S(2)	107.3 (6)	S(1)-S(2)-C(20)	106.2 (7)
S(1)-C(10)-C(11)	103.9 (12)	S(2)-C(20)-C(21)	110.2 (14)
S(1)-C(10)-C(12)	111.2 (13)	S(2)-C(20)-C(22)	111.8 (14)
S(1)-C(10)-C(13)	114.5 (12)	S(2)-C(20)-C(23)	106.0 (14)
C(11)-C(10)-C(12)	106.6 (15)	C(21)-C(20)-C(22)	109.3 (17)
C(11)-C(10)-C(13)	109.7 (16)	C(21)-C(20)-C(23)	110.5 (16)
C(12)-C(10)-C(13)	110.4 (15)	C(22)-C(20)-C(23)	109.1 (17)
C(10)-C(11)-C(14)	110.5 (16)	C(20)-C(21)-C(24)	109.1 (17)
C(10)-C(12)-C(15)	111.5 (17)	C(20)-C(22)-C(25)	110.2 (16)
C(10)-C(13)-C(16)	110.4 (14)	C(20)-C(23)-C(26)	108.6 (16)
C(11)-C(14)-C(17)	109.9 (17)	C(21)-C(24)-C(27)	110.4 (17)
C(11)-C(14)-C(19)	108.6 (17)	C(21)-C(24)-C(29)	111.2 (17)
C(17)-C(14)-C(19)	108.5 (17)	C(27)-C(24)-C(29)	106.1 (18)
C(12)-C(15)-C(17)	108.1 (16)	C(22)-C(25)-C(27)	109.5 (17)
C(12)-C(15)-C(18)	109.0 (16)	C(22)-C(25)-C(28)	107.8 (17)
C(17)-C(15)-C(18)	107.7 (16)	C(27)-C(25)-C(28)	108.3 (17)
C(13)-C(16)-C(18)	110.2 (15)	C(23)-C(26)-C(28)	108.5 (17)
C(13)-C(16)-C(19)	108.8 (15)	C(23)-C(26)-C(29)	113.2 (19)
C(18)-C(16)-C(19)	107.1 (15)	C(28)-C(26)-C(29)	107.8 (20)
C(14)-C(17)-C(15)	111.7 (17)	C(24)-C(27)-C(25)	110.4 (18)
C(15)-C(18)-C(16)	112.0 (15)	C(25)-C(28)-C(26)	110.3 (21)
C(14)-C(19)-C(16)	109.6 (17)	C(24)-C(29)-C(26)	109.9 (18)

[a] Estimated standard deviations in parentheses.

The value of the S–S torsional angle determined by X-ray crystallography in the present work, 110.5 (9)°, is in reasonably good agreement with the earlier calculated value (114°) for DAD.[1b] The previous molecular mechanics calculations also predicted the adamantyl groups to be slightly twisted from the perfectly staggered conformation,[19] although the computed rotation is smaller (1–4°) than that observed by X-ray crystallography (5–10°; see Figure 3).

It is noteworthy that the current force field produces a rather shallow energy minimum for twisting about the S–S bond.[1b,10] The correspondence between $\theta(\mathrm{CSSC})_{\mathrm{calcd}}$ and $\theta(\mathrm{CSSC})_{\mathrm{X\text{-}ray}}$ can be interpreted to mean that both the position of the torsional minimum and the shape of the potential energy surface are well represented by the calculations. On the other hand, if the actual rotational surface is indeed relatively flat and the gas-phase minimum is poorly reproduced by the force field, then the θ(CSSC) accord may be a result of crystal-packing forces having displaced the unperturbed minimum fortuitously to 111°. We prefer the first interpretation for the following reasons.

The force field estimated *trans*-disulfide barriers for CH_3SSCH_3, *t*-Bu–SS–*t*-Bu, and DAD are 7.0, 5.0, and 5.3 kcal/mol, respectively, while the corresponding cis barriers are calculated to be 10.6, 28.8, and 29.7 kcal/mol, respectively.[1b,10] The shapes of the modeled torsional potential energy surfaces for these RSSR derivatives are therefore quite similar. Further, both gas-phase *and* solid-state determinations of θ(CSSC) for acyclic dialkyl disulfides bearing primary carbons α to sulfur demonstrate that the S–S dihedral angle is bounded by the narrow range of 82–92°.[4,20] Tertiary dialkyl disulfides are not obviously encumbered with qualities causing them to deviate from this pattern. Thus, the concurrence between calculated and experimental θ(CSSC)'s for DAD would seem to be of the same quality as that observed for other dialkyl disulfides.[1b,17] Final resolution of this question will require much greater effort and, no doubt, necessitate a structural evaluation in the gas phase.[21]

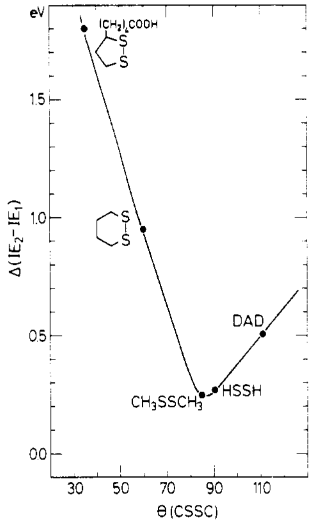

Figure 4. Experimental correlation between the CS–SC dihedral angle, θ(CSSC), and the sulfur lone-pair energy gap, $\Delta E(n_+ - n_-)$, for dialkyl disulfides. Except for DAD, the data have been taken from ref 23.

$\theta(\mathrm{CSSC})/\Delta E(n_+ - n_-)$ Correlation. The photoelectron spectra of dialkyl disulfides exhibit two low-energy ionizations. Within the applicability of Koopmans' theorem these have been assigned to the antibonding (n_-) and bonding (n_+) combinations of the high-lying sulfur lone electron pairs.[1b,22-25] By means of extended Hückel MO calculations on MeSSMe, Bock and Wagner suggested that the lone-pair energy gap, $\Delta E(n_+ - n_-)$, is dependent on the degree of torsion about the S–S bond.[22] Shortly thereafter, Guimon and Pfister-Guillouzo quantified the relationship by plotting $\Delta E(n_+ - n_-)$ against the experimentally determined values of θ(CSSC).[23] Although structural information was available only for disulfides with dihedral angles of up to 90°, the findings were nevertheless applied to *t*-Bu–SS–*t*-Bu by appealing to the predictions of the EHMO calculations.[22,23] The resulting angle, $\theta(\mathrm{CSSC}) \simeq 110°$, is identical with that suggested by CNDO/S calculations.[24]

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[19] See ref 1b, Figure 5a.

[20] For a fairly extensive survey of disulfide crystal structures, see H. E. Van Wart and H. A. Scheraga, *J. Phys. Chem.*, **80**, 1812 (1976).

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The present work in combination with the recently determined photoelectron spectrum of DAD[1b] allows tentative extension of the $\theta(CSSC)/\Delta E(n_+-n_-)$ correlation to 111° as depicted in Figure 4. It should be borne in mind that the one-point extrapolation beyond 90° is made with the reservations expressed in the previous section. Direct application of the revised curve to *t*-Bu-SS-*t*-Bu is somewhat tenuous since the literature values for $\Delta E(n_+-n_-)$ range from 0.60[23] to 0.65.[23,25a] Thus we have measured the spectrum once again as the average of several determinations. The result, $\Delta E(n_+-n_-) = 0.63$, implies $\theta(CSSC) = 121°$. Elaboration of the $\theta(CSSC)/\Delta E(n_+-n_-)$ relationship to larger values of the S-S dihedral angle awaits the availability of a suitable series of dialkyl disulfides.

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Additive Pummerer-Initiated Functionalization of Allylic Methyl Groups in Acrylic Acid Derived Systems

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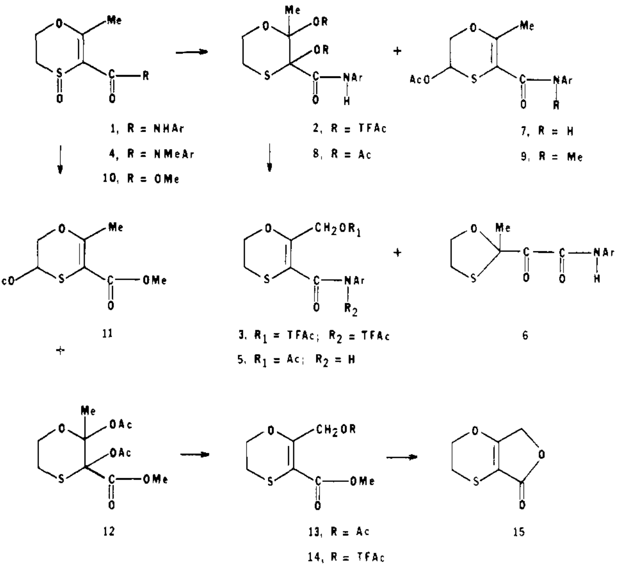
Elucidation of reaction parameters for the conversion of the additive Pummerer product 2,3-bis(trifluoroacetoxy)-2-methyl-1,4-oxathiane-3-carboxanilide (**2**) to *N*-(trifluoroacetyl)-5,6-dihydro-2-[(trifluoroacetoxy)methyl]-1,4-oxathiin-3-carboxanilide (**3**) was facilitated by substituting an acetic anhydride-acetic acid mixture for trifluoroacetic anhydride in the Pummerer reaction step and by investigating both sets of reaction conditions on 3-(carbomethoxy)-5,6-dihydro-2-methyl-1,4-oxathiin 4-oxide (**10**).

Carboxin (5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide) and structurally related carboxamides are well established as systemic fungicides which can effectively control various smuts and rust diseases.[1] The transformation (for gas-liquid chromatography purposes) of carboxin sulfoxide (**1**; an oxidative metabolite of carboxin) to *N*-(trifluoroacetyl)-5,6-dihydro-2-[(trifluoroacetoxy)methyl]-1,4-oxathiin-3-carboxanilide (**3**) by reaction with trifluoroacetic anhydride (TFAA) (Scheme I) has been reported previously.[2] This novel reaction provided access to previously unavailable 2-(oxymethyl)carboxin analogues for potential structure-activity relationship studies.[3] Mechanistically, it was determined that carboxin sulfoxide (**1**) on treatment with TFAA initially underwent an additive Pummerer reaction[4] to yield the bis(trifluoroacetoxy)-1,4-oxathiane **2**. This compound subsequently rearranged to the allylic trifluoroacetate **3**. Investigations regarding the mode of conversion from compound **2** to **3** suggested a concerted reaction with possible participation of the anilide group.

As a consequence of its potential synthetic utility, attempts to further elucidate reaction parameters for the allylic methyl functionalization step were undertaken. The first approach involved use of a less active acetylating agent (acetic anhydride) in order to enhance the possible isolation of previously undetected intermediates.[5] The second approach involved replacement of the anilide moiety in carboxin sulfoxide with a methyl ester group in order to establish the role, if any, of an active NH group.

Scheme I



Results and Discussion

Carboxin sulfoxide (**1**) in benzene containing a 2:1 mixture of acetic anhydride-acetic acid[5] was refluxed on a steam bath until TLC studies indicated complete reac-

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