

**E Z Stereoisomerization in Methylene bis-Dithiocarbamate and N,N,S-
Trimethyldithiocarbamate**


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Signature Page


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Abstract

Rates of rotation about the carbon-nitrogen partial double bond in N,N,S-trimethyldithiocarbamate (**1**) and methylene bis-dithiocarbamate (**2**) were measured by the dynamic NMR technique known as selective inversion recovery. Free energies of activation (ΔG^\ddagger) for the rotational barrier about the carbon-nitrogen partial double bond in compounds **1** and **2** were determined in a variety of solvents. Compound **1** was found to have a lower rotational barrier than compound **2**. As solvent polarity increased, an increase in rotational barrier was observed. Contrary to expectations, hydroxylic solvents lowered the rotational barrier for compounds **1** and **2** based on their increased solvent polarity and hydrogen bonding capabilities. These results have implications for determining switching rates in dithiocarbamate chiroptical switches.

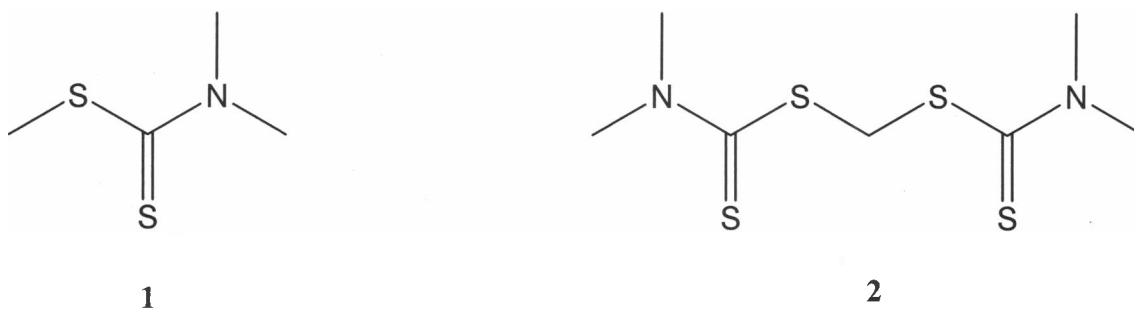
Figure 1: Compounds **1** and **2**

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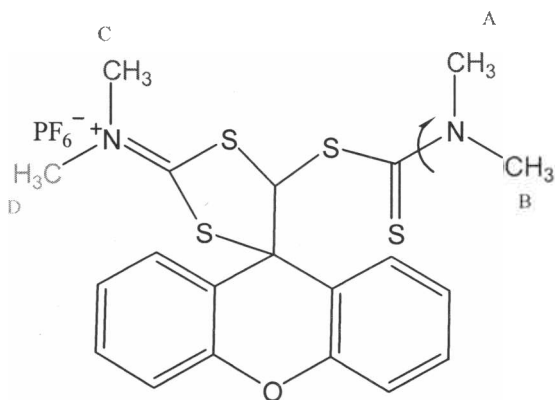
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Introduction

The potential use of a chiroptical switch (Figure 2) for information storage merits further investigation of the rates of rotation about the carbon-nitrogen partial double bond as well as the ring conversion the molecule undergoes^{1,2}. Because the physical properties of the compounds change significantly when the molecule converts from the R to the S configuration, the two enantiomers can be used to code for zeros and ones, as is done in current information storage devices. The chiroptical switch is designed to have a dipole moment in its natural state. When the molecule switches from the R to the S configuration the dipole moment switches to the opposite direction. This 180° flip would allow an external electric field to be applied, resulting in molecules with a dipole aligned with the field to be in a lower energy state. These differing energy states in turn could code for zeros and ones. The chiroptical switch would allow for more information to be stored in a smaller amount of space¹ than the current method used, which involves inducing dipole moments in molecules. By studying and understanding when this molecule switches/rotates, its presumed ability to store information in devices such as computers can be tested.

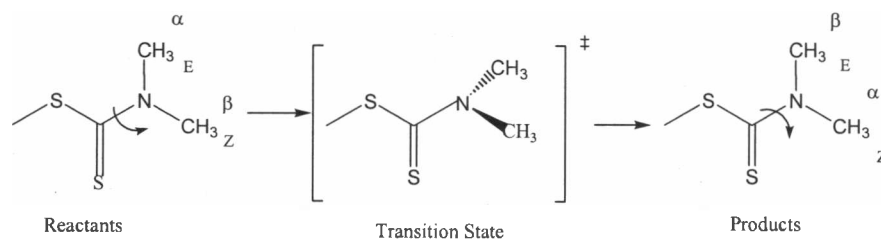
Figure 2: Chiroptical Switch



Because the chiroptical switch is a complex molecule I chose to study simpler dithiocarbamates in order to more fully understand the rate of rotation about the carbon-nitrogen partial double bond. The chiroptical switch has a higher rotational barrier about the carbon-nitrogen partial double bond than those of other dithiocarbamates^{3,4}. This could be due to the ring conversion that the molecule is undergoing. In my study, rates of rotation about the carbon-nitrogen partial double bond in N,N,S-trimethyldithiocarbamate (1) and methylene bis-dithiocarbamate (2) were measured by the dynamic NMR technique known as selective inversion recovery. This technique involves inverting one of the exchanging peaks while keeping the other exchanging peak aligned with the static magnetic field.

This inversion illustrates how a selectively excited population of nuclei can release energy and return to the lowest energy configuration. When the magnetic field is applied, the nuclei in one of the methyl groups are aligned opposite the magnetic field. Energy is released through the relaxation of the spins into an alignment with the magnetic field as well as through the rotation of the carbon-nitrogen partial double bond. This rotation is reversible, and results in degenerate, planar product and reactant (Figure 3).

Figure 3: Degenerate Chemical Exchange in Compound 1



As the carbon-nitrogen partial double bond rotates, the nuclei aligned with the magnetic field become antiphase. This causes the population of nucleons aligned with the

magnetic field to decrease, and in turn the intensity of the methyl Z peak decreases. As the population of excited nucleons relaxes and becomes aligned with the magnetic field again the signal of the methyl Z peak begins to increase. The intensity of the methyl E peak steadily increases due to chemical exchange. The time dependence of the intensities is complicated by spin-lattice relaxation effects, which can be accounted for by fitting the data to known equations³ (shown below).

$$I_E(t) = I_{E\infty} - C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t}$$

$$I_Z(t) = I_{Z\infty} - C_3 e^{-\lambda_1 t} + C_4 e^{-\lambda_2 t}$$

$$C_{1,2} = \delta I_{E\infty} ((R_Z - R_E \pm S) / 2) - \gamma I_{Z\infty} k$$

$$C_{3,4} = \frac{\delta I_{E\infty} k + \gamma I_{Z\infty} ((R_Z - R_E \pm S) / 2)}{S}$$

$$\lambda_{1,2} = \frac{(R_E + R_Z + 2k \pm S)}{2}$$

$$S = \sqrt{(R_E - R_Z)^2 + 4k}$$

R = spin lattice relaxation rate (1/T)

E_0, Z_0 = unperturbed intensities (intensities at infinity time)

E_t, Z_t = intensities at time t

γ & δ = corrections for imperfections that originate when pulsing does not return the E and Z magnetization to the $\pm z$ axis ($\gamma=2$ and $\delta=0$ for a perfect 90° pulse)³

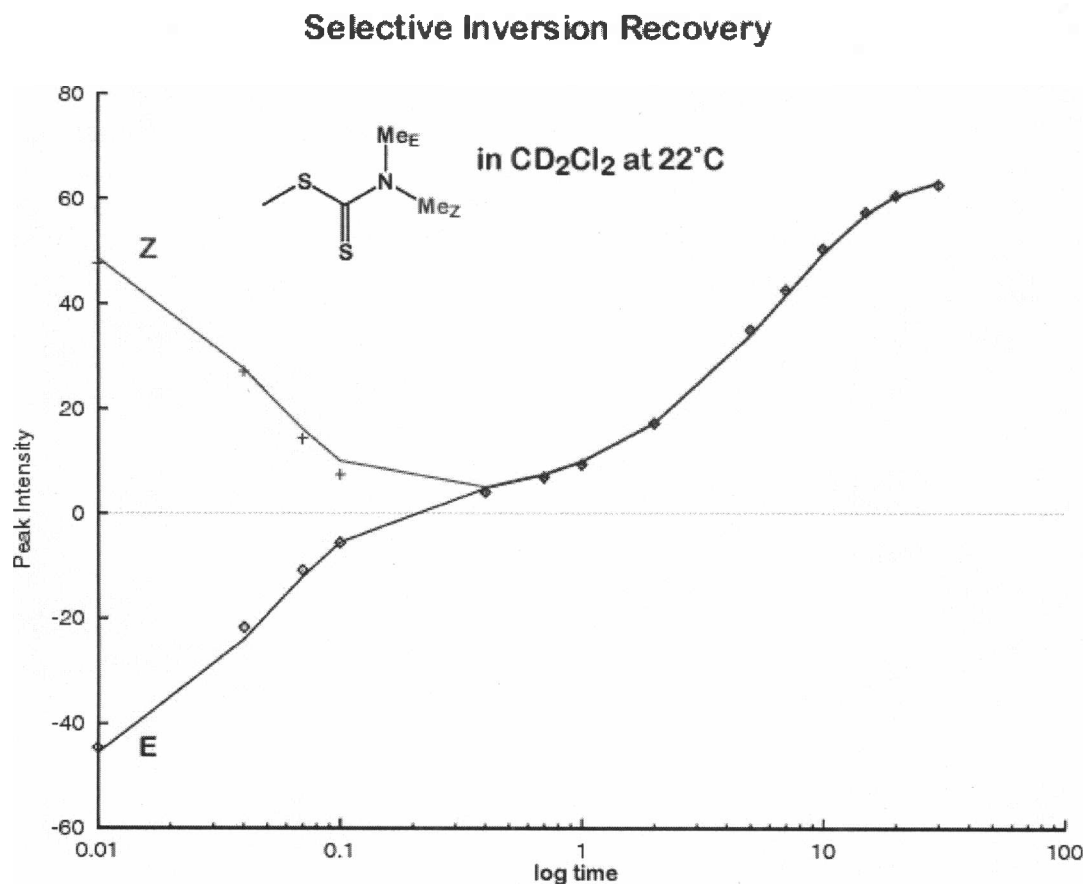
I = intensities

C = constant

Once the intensities had been extracted the mixing times and intensity values were entered into the FORTRAN computer program. The program used the equations above to fit the data. Seven parameters were fitted, three of which could be changed manually (T_1 's and k). The other four were changed by the computer in conjunction with the changes to the spin-lattice relaxation and k values. When a close fit was obtained through manual changing of the three parameters the computer could run a best fit program and determine the actual values of k and T_1 , which allowed for the

determination of ΔG^\ddagger . Below is an example of a typical graph (Figure 4) obtained through computer fitting.

Figure 4: Typical Graph Obtained Through Computer Fitting of Data.



In this study free energies of activation for compounds **1** and **2** were determined in a variety of solvents. The values were compared to those previously studied^{4,5}. I hypothesized that the rotational barrier of compound **2** would be higher than that of compound **1** because it more closely resembles the chiroptical switch itself. I also hypothesized that the rotational barriers of the compounds would increase with increased solvent polarity due to solvation effects. The additional knowledge gained from these

experiments might add to the current bank of information regarding the chiroptical switch.

Materials and Methods

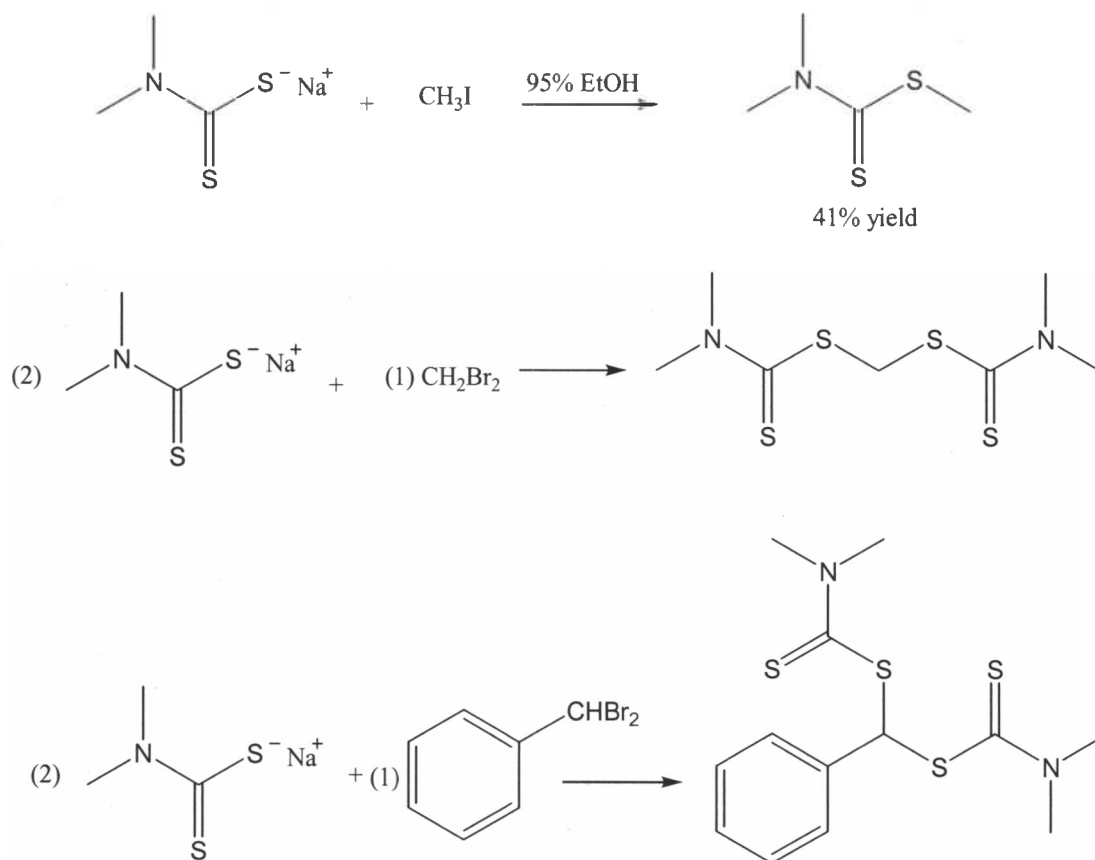
A. Synthesis

The general procedure outlined by C. E. Holloway¹ for synthesis of S-Methyl N,N-dimethyldithiocarbamate was followed: S-Methyl N,N-dimethyldithiocarbamate was synthesized by dropwise addition of 1.91 mL (4.349g, 0.0300 moles) of methyl iodide to a solution of 4.83g (.0270 moles) of sodium dimethyldithiocarbamate hydrate in 20mL of 95% ethanol in a 50mL round bottom flask. The mixture was stirred for twenty minutes and then 100mL of deionized water was added. The product was formed by a simple S_N2 reaction. This solution was extracted with ether (3x20mL). The ether extracts were combined and transferred into a 100mL round bottom flask and the ether removed at reduced pressure in a rotary evaporator. The flask was left overnight to allow more time for the ether to evaporate. Purification of the crude product was accomplished by recrystallization in pentane in a refrigerator at 4° C for two hours. The resulting crystals were filtered and weighed and a melting point, IR spectra, and NMR spectra were obtained for identification purposes. During filtration more S-Methyl N,N-dimethyldithiocarbamate precipitated out of solution, from which a second crop was purified by cold recrystallization from pentane. Yield = 41% (more product could be found in the mother liquor). mp 45°-46° C (Lit¹: 45 C). IR: 2916cm⁻¹ (CH stretch), 1508 cm⁻¹ (C=S stretch). ¹H NMR δ(ppm acetone-d₆), 3.52 (s, 3H, E-methyl), 3.39 (s, 3H, Z-methyl), 2.56 (s, 3H, S-methyl).

Dr. James Parakka and Dr. Robert Schumaker from California Molecular Electronics synthesized compounds 2 and 3. These compounds were synthesized in the

same fashion (Figure 5), in a S_N2 reaction with dibromomethane and dibromotoluene as the respective nucleophilic attackers.

Figure 5: Synthesis of Compounds 1, 2, and 3



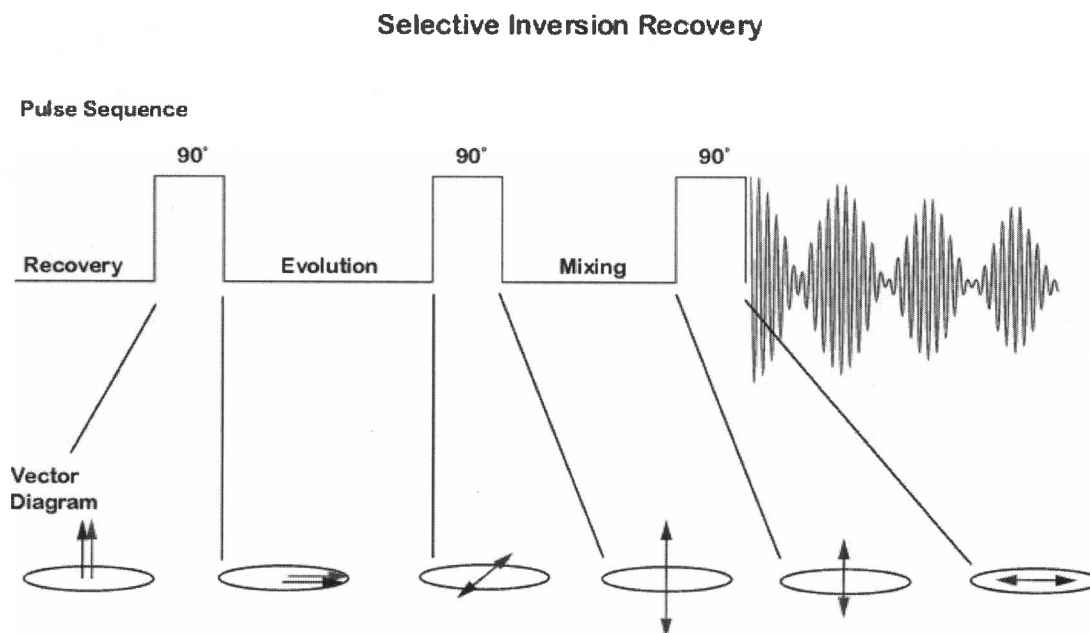
B. NMR Experiments

Compounds 1, 2, and 3 were dissolved into several different deuterated solvents in order to be analyzed by the NMR. These compounds include: benzene, bromobenzene, chloroform, methylene chloride, acetone, dimethylsulfoxide, DMF, isopropanol, ethanol, methanol. Approximately five milligrams of sample were dissolved in 0.5-.075mL of deuterated solvent, with the exception of the alcohols, in which compound 2 would not dissolve very well and as a result only 0.5-1.0 milligrams were dissolved. When a sample was ready for analysis, a routine proton spectrum was obtained in order to

optimize the lock system, optimize the magnetic field homogeneity (as verified by linewidths), and establish a constant temperature for the kinetic runs. The effect of ambient temperature fluctuation can be minimized by regulating the temperature. After these parameters were optimized the carrier frequency was moved to exactly halfway between the exchanging peaks. This was accomplished by the dof command, which reports the frequency of the individual peaks (the methyl peaks in this case), calculating the difference between the two peaks, dividing that difference by two and then adding that value to the upfield peak. The center of the spectrum (tof) can then be set to that value and the parameters of that experiment moved to a new experiment. In this new experiment the spectral window is narrowed so as to include only spectral lines and not the large expanse of flat baseline outside the region of interest.

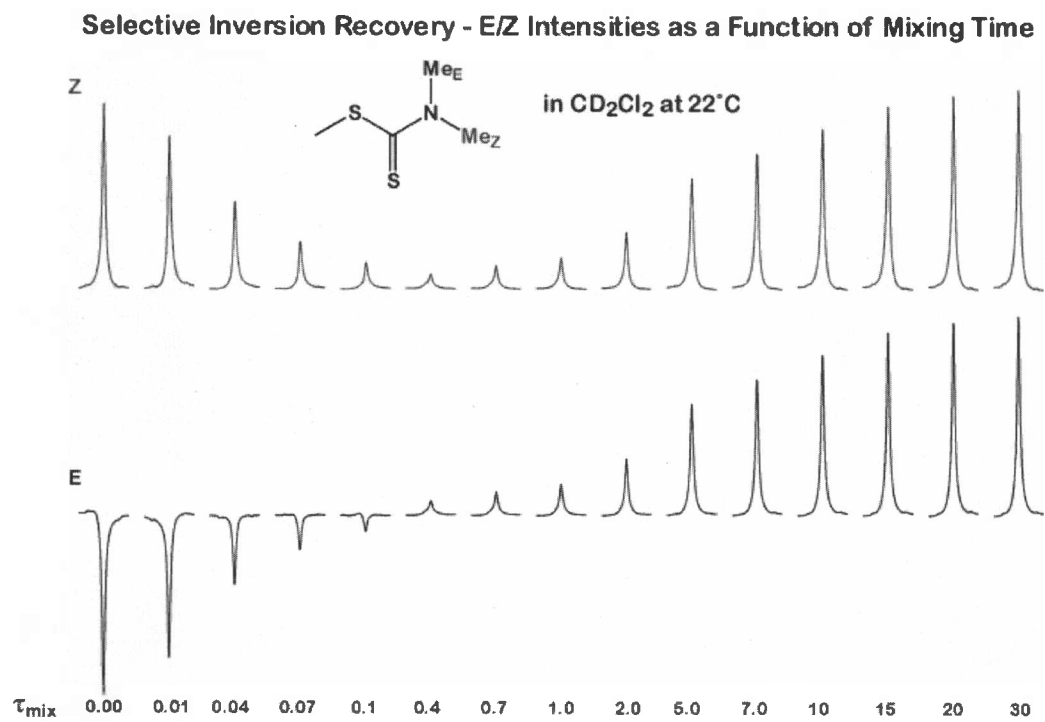
The ^1H pulse (Figure 6) sequence is then introduced through a file titled exsy1D.

Figure 6: Pulse Sequence Applied to Compounds 1, 2, and 3



The sequence works as follows. The first delay, d_1 , is the time allowed for all of the protons to relax back into their equilibrium intensities (as determined by peak height) before the sequence starts another repetition. In this experiment d_1 lasted for twenty seconds, approximately five times the estimated spin-lattice relaxation. An oscillating magnetic field pulse, represented by p_w is then applied perpendicular to the static magnetic field for eleven microseconds. This pulse causes spins oriented along the z-axis to be tipped ninety degrees into the xy plane. Once in the xy plane the protons are given time to evolve or precess (d_2) according to their chemical shift anisotropy. The spins precess at a rate proportional to their distance from the carrier frequency. In this experiment d_2 varied with each compound and each solvent, and was calculated by dividing one fourth of a revolution by the difference between the two peaks, designated δ , divided by two ($d_2 = 0.25 \text{ cycles}/(\delta/2)\text{cycles/second}$). At the end of the evolution period the E and Z spins are still located in the xy plane, but are antiphase (pointing in opposite directions). Thereafter another ninety degree oscillating magnetic field pulse is applied for 11 microseconds. This pulse returns the spins to the positive or negative z axis with one up and one down. A variable mixing time follows during which the spins equilibrate through spin-lattice relaxation (T_1) and chemical exchange (k). Mixing times varied according to compound and solvent, but typical values were (in seconds); 0, .005, .01, .02, .04, .07, .1, .2, .5, 1, 2, 5, 10, 20, 30. After a given mixing time a third ninety degree pulse was applied to bring magnetization back into the xy plane where it can be detected. Thus my data were collected and analysis could begin. A typical spectrum obtained from this experiment is shown below.

Figure 7: Typical Spectrum Obtained from an Experiment.



Results

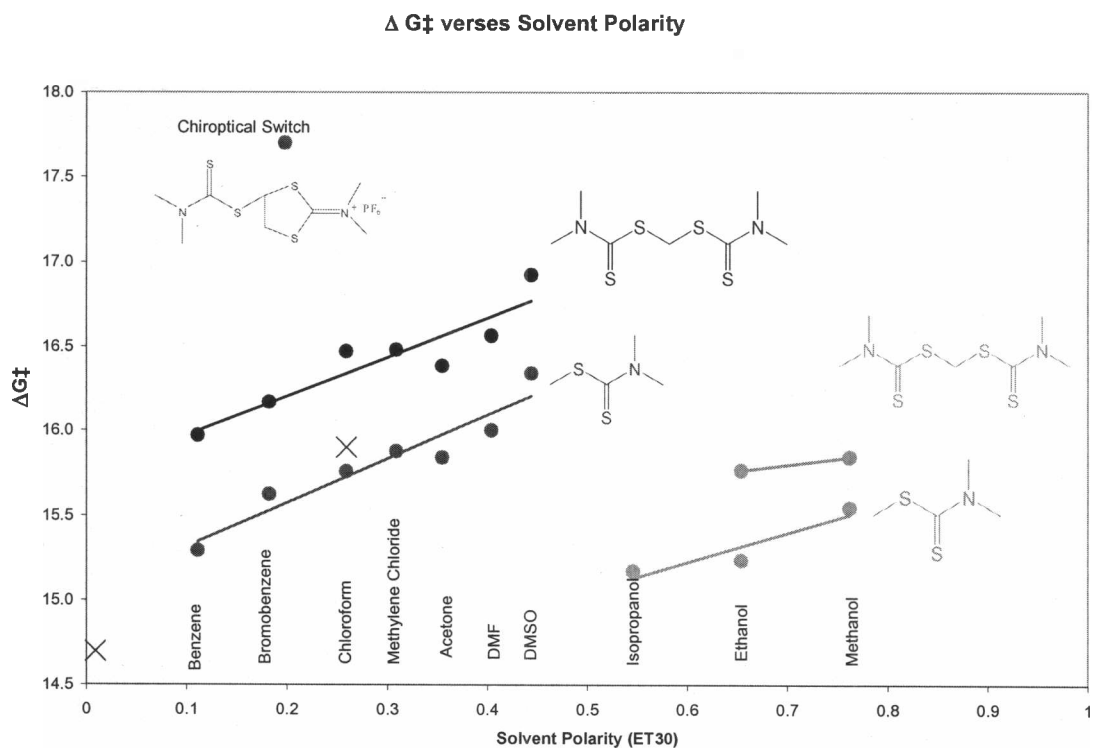
The rotational barriers of compounds **1** and **2** increased as solvent polarity increased in both the nonhydroxylic and the hydroxylic solvents (Figure 8). The rotational barriers of compounds **1** and **2** decreased as the solvent was changed from nonhydroxylic to hydroxylic. Also below are the ΔG^\ddagger and k values (Table 1) calculated from the E and Z intensities of the methyl peaks (appendix A). Rotational barriers for compound **1** varied from 15.23 kcal/mol to 16.34 kcal/mol, while rotational barriers for compound **2** varied from 15.76 kcal/mol to 16.93 kcal/mol. The ΔG^\ddagger values for the rotational barrier about the carbon-nitrogen partial double bond in compound **1** were lower than those of compound **2**.

Table 1: ΔG^\ddagger Values/Rate Constants (k) of Compounds 1 and 2 in Various Solvents.

Cmpd	Solvent	$E_T(30)_1$	Temp (°C)	k (s ⁻¹)	k _{int} (s ⁻¹)	ΔG^\ddagger (kcal/mol)
1	C ₆ D ₆	0.111	5	5.6 ± 0.1	5.6 ± 0.1	15.29 ± 0.01
2	C ₆ D ₆	0.111	5	3.3 ± 0.2	1.64 ± 0.08	15.97 ± 0.03
1	C ₆ D ₅ Br	0.182	22	17 ± 1	17 ± 1	15.62 ± 0.04
2	C ₆ D ₅ Br	0.182	22	13.1 ± 0.2	6.6 ± 0.2	16.17 ± 0.02
1	CDCl ₃	0.259	15	6.7 ± 0.1	6.7 ± 0.1	15.76 ± 0.01
2	CDCl ₃	0.259	15	3.9 ± 0.2	1.93 ± 0.09	16.47 ± 0.03
1	CD ₂ Cl ₂	0.309	22	10.8 ± 0.3	10.8 ± 0.3	15.88 ± 0.02
2	CD ₂ Cl ₂	0.309	22	7.7 ± 0.3	3.8 ± 0.2	16.48 ± 0.03
1	acetone-d ₆	0.355	25	15.2 ± 0.4	15.2 ± 0.4	15.84 ± 0.02
2	acetone-d ₆	0.355	25	12.1 ± 0.4	6.0 ± 0.2	16.39 ± 0.02
1	DMF-d ₇	0.404	5	1.55 ± 0.05	1.55 ± 0.05	16.00 ± 0.02
2	DMF-d ₇	0.404	5	1.12 ± 0.04	.56 ± 0.02	16.56 ± 0.02
1	DMSO-d ₆	0.444	25	6.5 ± 0.5	6.5 ± 0.5	16.34 ± 0.05
2	DMSO-d ₆	0.444	25	4.9 ± 0.3	2.4 ± 0.1	16.93 ± 0.04
1	isopropanol-d ₈	0.546	10	11.5 ± 0.5	11.5 ± 0.5	15.17 ± 0.03
1	ethanol-d ₆	0.654	10	10.3 ± 0.5	10.3 ± 0.5	15.24 ± 0.03
2	ethanol-d ₆	0.654	10	8.0 ± 0.7	4.0 ± 0.3	15.77 ± 0.05
1	methanol-d ₄	0.762	22	18.9 ± 0.9	18.9 ± 0.9	15.55 ± 0.03

¹Normalized $E_T(30)$ values taken from Reichardt, C. Solvents in and Solvent Effects in Organic Chemistry, 2nd ed; VCH: Weinheim, 1988 p 365-371.

Figure 8₂: Graph of the Effects of Solvent Polarity.



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²The graph has two x marks on it. These x marks represent rotational barriers measured by Lemire⁵ in a smaller, similar study. Also shown on this graph is the rotational barrier of the chiroptical switch².

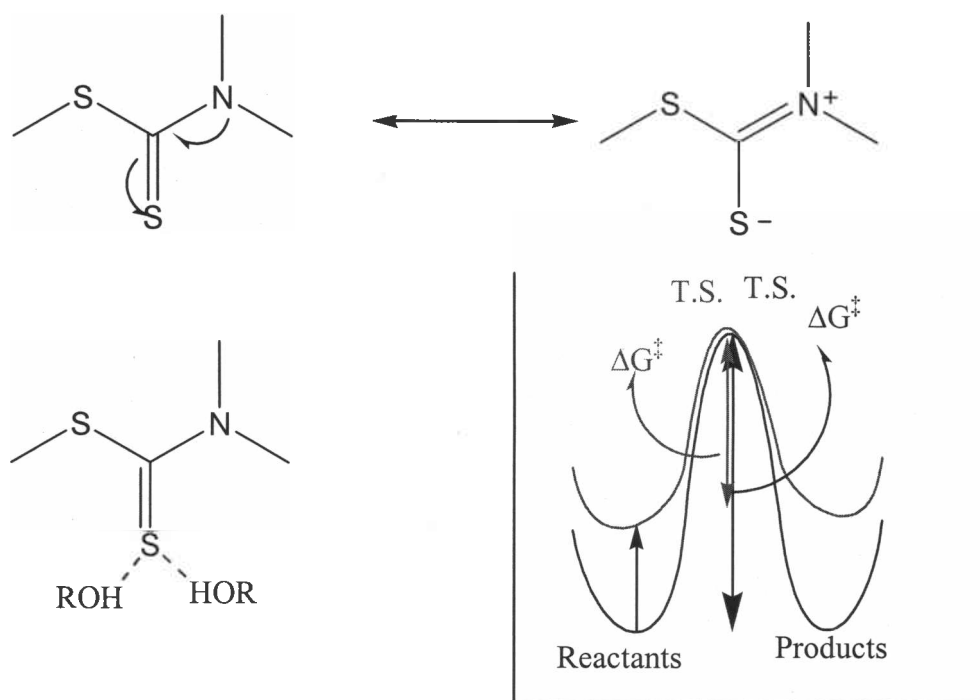
Discussion

Values for solvent effect calculated here (Figure 7) compare reasonably with those of Holloway and Lemire⁵. Compound **1** most likely has lower rotational barriers than either compound **2** or the chiroptical switch due to electronic effects. The electrons on the sulfur in the second dithiocarbamate group in compound **2** are most likely drawn towards the bridging carbon. This withdrawing action increases the occurrence of the carbon-nitrogen double bond and therefore increases the rotational barrier. The increase in rotational barrier in compound **2** may also be due to steric interference resulting from the tetrahedral shape of the bridgehead carbon. The presence of more electronegative atoms in the chiroptical switch may be what causes the rotational barrier of the molecule to be higher still than those of compounds **1** and **2**. Further investigation into the cause of the increase in rotational barriers, including molecular modeling, could confirm these speculations. Once the exact reason for this increase is known, the effect it has on the ring conversion of the molecule can be better understood.

As polarity increased in the nonhydroxylic solvents rotational barriers in both compounds **1** and **2** increased and the rate of rotation about the carbon-nitrogen partial double bond decreased. This was a result of the increased bipolar resonance structure, which increases the double bond character of the carbon-nitrogen bond and therefore slows rotation. The hydroxylic solvents lowered the rotational barriers instead of increasing them as was expected. Because the hydroxylic solvents were more polar than the nonhydroxylic solvents (higher $E_T(30)$ values) it was expected that they would continue to increase the rotational barriers. This unexpected decrease in rotational barriers was a result of

solvation. Hydrogen bonding occurred between the sulfur and the alcohol groups, causing steric hinderance and in turn causing the sulfur-carbon-nitrogen portion of the molecule to become nonplanar. This nonplanar conformation is higher in energy and so the energy of the reactants is raised and ΔG^\ddagger is in turn lowered (Figure 9).

Figure 9: Effect of Hydroxylic Solvents on Rotational Barriers.



The knowledge gained from studying compounds **1** and **2** in a variety of solvents helps to illustrate some of the reasons for the rotational barrier about the carbon-nitrogen partial double bond in dithiocarbamates. A more extensive study would allow for more complete knowledge and would perhaps provide scientists with criteria for rotational barriers about this bond. With this in mind, the determination of what makes the ring in the parent compound (chiroptical switch) undergo ring conversion could be studied and

the effects of the rotation about the carbon nitrogen double bond on this conversion could be taken into account.

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Appendix A

Intensities of E and Z Methyl Peaks

Table 1

Intensities of E and Z Methyl Peaks in N,N,S-Trimethyldithiocarbamate (Acetone-d₆)

#	τ_{mix} (s)	I _E	I _Z
1	0	-43.85	46.30
2	.005	-37.44	39.34
3	.01	-31.30	33.94
4	.02	-22.09	27.10
5	.04	-9.03	16.80
6	.07	-1.14	10.22
7	.1	4.37	8.69
8	.2	7.72	8.19
9	.5	10.34	10.65
10	1	14.93	15.28
11	2	20.78	20.78
12	5	33.99	34.70
13	10	47.46	46.60
14	20	57.34	56.66
15	30	59.60	58.66

Table 2

Intensities of E and Z Methyl Peaks in Methylene Bis-Dithiocarbamate (Acetone-d₆)

#	τ_{mix} (s)	I _E	I _Z
1	0	-47.58	50.69
2	.005	-44.79	46.72
3	.01	-40.82	44.69
4	.02	-38.14	39.70
5	.04	-27.36	33.21
6	.07	-17.40	22.58
7	.1	-12.28	16.28
8	.2	-1.28	7.26
9	.5	6.61	6.48
10	1	11.65	11.32
11	2	19.85	19.41
12	5	34.84	34.75
13	10	45.18	45.15
14	20	50.25	50.30
15	30	50.89	50.85

Table 3
Intensities of E and Z Methyl Peaks in N,N,S-Trimethyldithiocarbamate (DMSO-d₆)

#	τ_{mix} (s)	I _E	I _Z
1	0	-10.92	11.04
2	.005	-9.43	11.32
3	.01	-8.62	10.43
4	.02	-7.95	8.12
5	.04	-5.95	6.79
6	.07	-4.23	5.13
7	.1	-2.51	3.87
8	.2	-.03	2.18
9	.5	1.53	1.98
10	1	2.66	3.24
11	2	4.69	5.25
12	5	8.26	8.94
13	10	10.58	11.30
14	20	11.57	12.30
15	30	11.71	12.46

Table 4
Intensities of E and Z Methyl Peaks in Methylene Bis-Dithiocarbamate (DMSO-d₆)

#	τ_{mix} (s)	I _E	I _Z
1	0	-51.1	59.28
2	.005	-49.93	58.32
3	.01	-47.97	57.52
4	.02	-46.92	54.63
5	.04	-39.12	51.70
6	.07	-29.81	44.62
7	.1	-25.89	40.32
8	.2	-11.93	30.42
9	.5	9.89	23.24
10	1	22.74	28.75
11	2	34.38	40.06
12	5	45.53	51.91
13	10	48.64	55.11
14	20	50.30	56.67
15	30	50.50	56.86

Table 5
Intensities of E and Z Methyl Peaks in N,N,S-Trimethyldithiocarbamate (CDCl₃)

#	τ_{mix} (s)	I _E	I _Z
1	0	-45.63	47.21
2	.01	-39.48	41.67
3	.04	-25.65	28.43
4	.07	-16.51	19.93
5	.1	-8.64	14.40
6	.4	5.46	5.84
7	.7	8.78	8.88
8	1	11.63	11.75
9	2	19.94	20.08
10	5	35.53	35.74
11	7	41.20	41.41
12	10	45.75	45.99
13	12	47.42	47.65
14	15	48.77	49.07
15	20	49.82	50.05

Table 6
Intensities of Methyl E and Z Peaks in Methylene Bis-Dithiocarbamate (CDCl₃)

#	τ_{mix} (s)	I _E	I _Z
1	0	-55.19	55.97
2	.0	-50.55	54.12
3	.04	-43.80	47.16
4	.07	-38.28	42.95
5	.1	-32.41	38.59
6	.2	-17.40	27.90
7	.4	0.83	18.79
8	.5	6.45	17.41
9	.75	14.88	18.03
10	1	19.94	20.69
11	2	32.86	32.46
12	5	49.56	49.26
13	10	56.80	56.45
14	20	58.66	58.26
15	30	59.15	58.63

Table 7

**Intensities of E and Z Methyl Peaks in N,N,S-Trimethyldithiocarbamate
(Benzene-d₆)**

#	τ_{mix} (s)	I _E	I _Z
1	0	-29.54	30.46
2	.005	-26.48	28.68
3	.01	-25.92	27.07
4	.02	-22.46	24.13
5	.04	-17.68	19.63
6	.07	-11.75	14.22
7	.1	-8.33	10.65
8	.2	-1.10	4.76
9	.5	3.65	3.20
10	1	6.67	6.00
11	2	11.35	10.72
12	5	20.77	20.00
13	10	27.49	26.88
14	20	30.62	30.03
15	30	30.99	30.34

Table 8

Intensities of E and Z Methyl Peaks in Methylene Bis-Dithiocarbamate (Benzene-d₆)

#	τ_{mix} (s)	I _E	I _Z
1	0	-30.33	32.25
2	.01	-28.81	31.22
3	.04	-24.03	27.92
4	.07	-20.69	26.11
5	.1	-17.54	23.82
6	.2	-12.46	18.47
7	.4	-1.70	13.08
8	.5	1.63	11.97
9	.75	7.01	11.32
10	1	10.78	12.38
11	2	17.97	18.29
12	5	26.79	27.29
13	10	30.16	30.76
14	20	30.81	31.30
15	30	30.60	31.05

Table 9

**Intensities of E and Z Methyl Peaks in N,N,S-Trimethyldithiocarbamate
(Methanol-d₄)**

#	τ_{mix} (s)	I _E	I _Z
1	0	-45.94	47.75
2	.005	-39.03	41.17
3	.01	-31.31	32.73
4	.03	-14.58	14.70
5	.05	-5.32	8.20
6	.1	1.76	4.05
7	.5	6.54	6.42
8	1	11.08	10.72
9	3	25.08	24.45
10	5	34.84	34.45
11	10	47.53	46.78
12	15	52.74	51.61
13	20	54.49	53.30
14	25	55.19	53.98
15	30	55.30	54.10

Table 10

**Intensities of E and Z Methyl Peaks in Methylene Bis-Dithiocarbamate
(Methanol-d₄)**

#	τ_{mix} (s)	I _E	I _Z
1	0	-30.72	31.64
2	.01	-26.91	27.70
3	.04	-14.97	17.28
4	.07	-8.79	13.17
5	.1	-4.80	7.31
6	.2	2.20	4.12
7	.4	4.62	4.99
8	.7	7.31	7.49
9	1	9.68	9.47
10	2	15.55	16.03
11	5	26.23	26.77
2	10	31.94	32.19
13	15	33.36	32.99
14	20	33.84	33.60
15	30	33.44	33.86

Table 11

**Intensities of E and Z Methyl Peaks in N,N,S-Trimethyldithiocarbamate
(Ethanol-d₆)**

#	τ_{mix} (s)	I _E	I _Z
1	0	-50.93	50.95
2	.005	-41.71	47.40
3	.01	-37.48	42.94
4	.03	-24.72	29.25
5	.05	-13.72	21.40
6	.1	-4.56	9.8
7	.25	4.25	4.86
8	.5	7.76	7.64
9	.75	10.46	10.46
10	1	13.36	13.26
11	3	29.66	29.64
12	5	39.25	39.28
13	10	49.69	49.74
14	20	53.24	53.25
15	30	53.20	53.34

Table 12

Intensities of E and Z Methyl Peaks in Methylene Bis-Dithiocarbamate (Ethanol-d₆)

#	τ_{mix} (s)	I _E	I _Z
2	.01	-10.32	12.27
3	.02	-8.91	11.24
4	.04	-7.03	9.87
6	.1	-3.07	7.01
7	.2	-0.19	4.01
8	.4	2.71	3.27
9	.7	4.46	4.40
10	1	5.69	5.63
11	2	8.36	8.56
12	5	11.18	12.00
13	10	11.78	12.96
14	20	11.64	13.09
15	30	11.80	13.22

Table 13

**Intensities of E and Z Methyl Peaks in N,N,S-Trimethyldithiocarbamate
(Isopropanol-d₈)**

#	τ_{mix} (s)	I _E	I _Z
1	0	-51.76	59.90
2	.005	-48.68	55.15
3	.01	-43.72	50.37
4	.03	-23.33	31.09
5	.05	-13.27	22.38
6	.1	-0.32	10.68
7	.25	8.75	8.82
8	.75	18.29	18.01
9	1	21.96	21.92
10	3	44.91	44.74
11	5	56.81	55.66
12	10	66.82	66.50
13	15	69.01	68.80
14	20	69.37	69.10
15	30	69.53	69.34

Table 14

Intensities of E and Z Methyl Peaks in N,N,S-Trimethyldithiocarbamate (CD₂Cl₂)

#	τ_{mix} (s)	I _E	I _Z
1	0	-57.19	57.84
2	.01	-44.63	47.58
3	.04	-21.73	27.10
4	.07	-10.77	14.43
5	.1	-5.50	7.50
6	.4	4.10	4.25
7	.7	6.98	6.97
8	1	9.37	9.46
9	2	17.21	17.36
10	5	34.94	34.90
11	7	42.53	42.58
12	10	50.31	50.33
13	15	57.32	57.38
14	20	60.52	60.59
15	30	62.59	62.71

Table 15

Intensities of E and Z Methyl Peaks in Methylene Bis-Dithiocarbamate (CD₂Cl₂)

#	τ_{mix} (s)	I _E	I _Z
1	0	-32.64	33.04
2	.01	-31.17	30.39
3	.04	-21.02	24.64
4	.07	-17.10	20.70
5	.1	-12.58	17.11
6	.2	-3.42	9.58
7	.4	3.12	5.94
8	.5	4.61	5.82
9	.75	6.88	6.97
10	1	8.77	8.66
11	2	14.48	14.54
12	5	24.51	24.67
13	10	30.66	30.93
14	20	33.28	33.60
15	30	33.66	33.95

Table 16

Intensities of E and Z Methyl Peaks in N,N,S-Trimethyldithiocarbamate (DMF)

#	τ_{mix} (s)	I _E	I _Z
1	0	-46.73	45.25
2	.01	-43.43	44.09
3	.04	-39.73	39.81
4	.07	-37.44	36.97
5	.1	-33.16	33.51
6	.2	-20.77	26.30
7	.4	-7.45	16.26
8	.5	-3.47	14.08
9	.75	4.46	11.92
10	1	7.80	12.15
11	2	17.46	18.75
12	5	32.39	34.07
13	10	42.41	44.28
14	20	46.52	48.62
15	30	46.98	48.99

Table 17

Intensities of E and Z Methyl Peaks in Methylene Bis-Dithiocarbamate (DMF)

#	τ_{mix} (s)	I_E	I_Z
1	0	-33.70	35.24
2	.05	-30.72	33.48
3	.1	-26.00	32.15
4	.5	-7.48	23.10
5	.75	-0.18	20.80
6	1	5.53	20.03
7	1.25	10.04	19.75
8	1.5	13.30	20.10
9	1.75	15.69	20.48
10	2	17.76	21.23
11	2.5	20.54	22.70
12	5	26.92	28.32
13	10	29.83	31.39
14	20	30.74	32.30
15	30	30.55	32.12

Table 18

Intensities of E and Z Methyl Peaks in N,N,S-Trimethyldithiocarbamate (Bromobenzene-d₅)

#	τ_{mix} (s)	I_E	I_Z
1	0	-35.42	35.53
2	.01	-31.11	30.13
3	.04	-21.04	26.21
4	.07	-19.06	17.77
5	.1	-7.01	10.22
6	.2	-1.42	5.74
7	.4	0.55	3.49
8	.5	2.64	3.15
9	.75	4.99	5.26
10	1	8.80	9.11
11	2	14.84	14.87
12	5	26.00	25.85
13	10	33.77	33.33
14	20	37.19	36.68
15	30	37.55	37.17

Table 19

**Intensities of E and Z Methyl Peaks in Methylene Bis-Dithiocarbamate
(Bromobenzene-d₅)**

#	τ_{mix} (s)	I _E	I _Z
1	0	-30.15	32.55
2	.01	-25.67	28.79
3	.04	-15.69	20.27
4	.07	-10.33	14.04
5	.1	-5.58	10.24
6	.2	2.01	5.90
7	.4	6.69	6.84
8	.5	7.99	8.00
9	.75	10.76	10.77
10	1	13.19	13.25
11	2	20.32	20.52
12	5	28.90	29.22
13	10	31.80	32.19
14	20	32.62	33.01
15	30	32.65	33.08