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Dynamic NMR Studies of a Potential Chiroptical Switch Based on Dithiocarbamate–Iminodithiolane Interconversion

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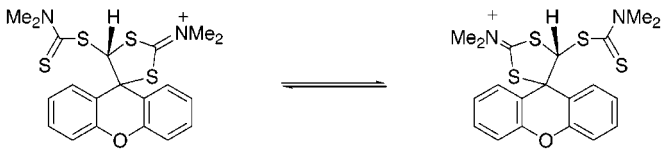
ABSTRACT



Variable temperature NMR spectra of the chiral spiro[(4-*N*,*N*-dimethyldithiocarbamato)-(2-*N*,*N*-dimethylimino)-1,3-dithiolane-5,9′-xanthene] show complex dynamics including degenerate interconversion of the dithiocarbamate and iminodithiolane groups. The rate of this switching process can be controlled by chemical modification: the analogous spiro[dithiolane-fluorene] derivative shows no interconversion. These novel materials have potential application as molecular switching elements in information storage devices.

Development of materials for high-density information storage and for miniaturization of switching devices is one of the major challenges in science and engineering.[1] Organic molecules are particularly attractive targets for these new materials. A molecular switch must exist in two isomeric forms corresponding to binary 0 and 1, show thermal irreversibility so that stored information is not lost at room temperature, have some nonthermal mechanism to drive the interconversion, be fatigue-resistant, and have a mechanism whereby the state can be read nondestructively.[2] Among the many organic compounds that possess photoreversible bistability and high thermal barriers, only a few are capable of nondestructive read-out, since the electronic absorption band that is used for detection is often identical to that used to promote isomerization. One approach to overcome this difficulty uses chiral compounds whose configuration inverts simultaneously with the photochromic isomerization.[2] The interconversion of isomeric states can be driven at one wavelength, λ_{write}, and the chirality read at a different probe wavelength, λ_{read}, using optical rotation, thereby avoiding destructive read-out. The photochromic modulation of known switches typically relies on cis−trans isomerization, photocyclization, or helix reversal processes. We report here a new molecular switch concept based on the degenerate valence bond isomerization in the chiral 4-*N*,*N*-dimethyldithiocarbamato-2-*N*,*N*-dimethylimino-1,3-dithiolane cation (**1**):[3]

S-**1** *R*-**1**

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(1) For a recent review, see special thematic issue: Photochromism: Memories and Switches. Irie, M., Ed. *Chem. Rev.* **2000**, *100*, 1683−1890. *Photoreactive Materials for Ultrahigh-Density Optical Memory*; Irie, M. Ed.; Elsevier: Amsterdam, 1994.

(2) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789.

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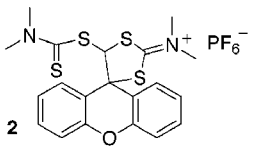
This structure has both an optically active center and a substantial dipole moment. Substitution of suitable chromophores at the 5 position of **1** is expected to yield light-activated switching between *R* and *S* states via the prochiral intermediate or transition state. The preferential existence of one or the other enantiomeric states will be controlled by the presence of an external electric field. Thus the influence of both light and directional field on these molecules, which we term Chiropticenes, will result in reversal of both the chirality as well as the dipole orientation.[4] One of the key requirements of molecular switches is a high thermal barrier to interconversion between the two distinct states. This can be investigated by means of variable temperature NMR studies. We report in this paper the thermal stability, stereoisomerization, and chemical control of switching for model compound **1** and its xanthenyl and fluorenyl derivatives, **2** and **3**.



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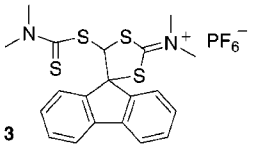

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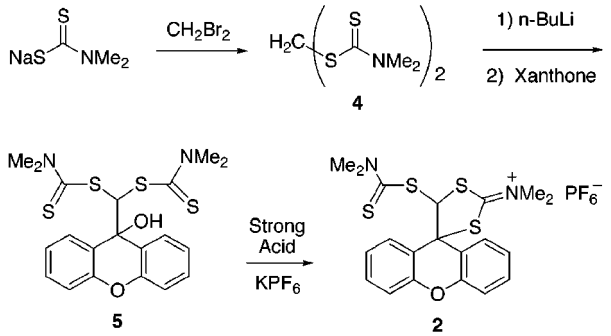
Compound **1** was synthesized in one step from 1,1,2-tribromoethane and sodium dimethyldithiocarbamate followed by anion exchange with KPF_6.[3] Compounds **2** and **3**



were synthesized by the general protocol outlined above. For example, lithiation of the known methylene(bisdimethyldithiocarbamate)[5] **4** followed by quenching with xanthone yielded tertiary alcohol **5**. Subsequent dehydration and cyclization promoted by strong acids (HCl, $HClO_4$, pTSA, or camphorsulfonic acid) followed by anion exchange using KPF_6 gave **2**. Similarly, the fluorenyl analogue **3** was prepared employing 9-fluorenone in the first step and $HClO_4$ in the cyclization sequence.

At room temperature the 400 MHz ^{1}H NMR spectrum of **1** in anisole-d_8 shows four unique methyl peaks (Figure 1).[6]

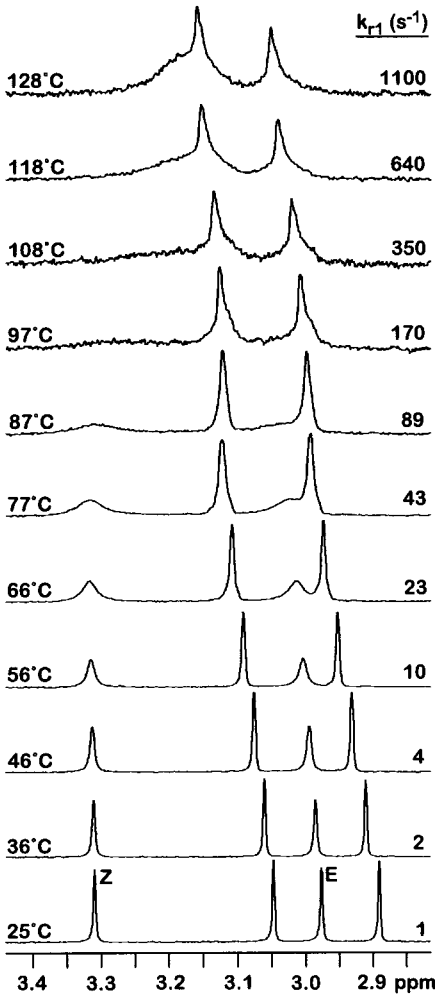


Figure 1. ^{1}H NMR (400 MHz) spectra for *N*-methyl region of **1** in anisole-d_8 showing the exchange of the dithiocarbamate *N*-methyls.

As temperature is raised the two dithiocarbamate methyl peaks broaden, coalesce near 108 °C, and then begin to resharpen. An Eyring plot of the rate constants derived from line shape analysis[7] gave a $\Delta G^{\ddagger} = 17.7 \pm 0.2$ kcal/mol at 25 °C. This is slightly higher than 15 kcal/mol rotational barriers seen in other alkylated dithiocarbamates.[8] Significantly, no other exchange is seen among the methyl groups,[9]

(3) Schumaker, R. R. Optoelectronic Tautomeric Compositions. U.S. Patent 5,237,067, August 17, 1993.

(4) (a) Hutchison, K. A.; Parakka, J. P.; Kesler, B. S.; Schumaker, R. R. Chiropticenes: Molecular Chiroptical Switches for Optical Data Storage. In *Micro- and Nano-photonic Materials and Devices*; Perry, J. W., Scherer, A., Eds.; *Proc. SPIE-Int. Soc. Opt. Eng.* 3937, **2000**, 64−71. (b) Parakka, J. P.; Schumaker, R. R.; Kesler, B. S.; Thoburn, J. D. Molecular-Based Chiroptical Dipole Switches. In *Optical Engineering for Sensing and Nanotechnology*; Iwata, K., Ed.; *Proc. SPIE-Int. Soc. Opt. Eng.* 4416, **2001**, 301−304.

(5) Nakai, T.; Okawara, M. *Chem. Lett.* **1974**, 731.

(6) Peak assignments were made based on the relative rates of exchange. E & Z peak assignments alkyl dithiocarbamates are the reverse of those in amides: Dahl, B. M.; Nielsen, P. H. *Acta Chem. Scand., Ser. B* **1974**, *B28*, 1091.

(7) Rate constants were obtained by piping calculated spectra from DNMR5 and the experimental spectra into GNUPOT3.4 for interactive iteration of parameters until the best fit was obtained. Stephenson, D. S.; Binsch, G. *DNMR5: Iterative Nuclear Magnetic Resonance Program for Unsaturated Exchange-Broadened Band shape, QCPE. 569*. Binsch, G. *J. Am. Chem. Soc.* **1969**, *91*, 1304.

(8) Holloway, C. E.; Gitlitz, M. H. *Can. J. Chem.* **1967**, *45*, 2659. Lemire, A. E.; Thompson, J. C. *Can. J. Chem.* **1975**, *53*, 3732.

indicating that the parent compound **1** does not undergo switching of the iminodithiolane and dithiocarbamate. Although **1** appears to have the essential high thermal barrier, it lacks the chromophore necessary for light-induced switching. We therefore undertook studies on model compounds **2** and **3**.

The dynamics of Chiropticene **2** are significantly more complex, as indicated by its variable temperature ^{1}H NMR spectra in C_6D_5Br (Figure 2). At room temperature four

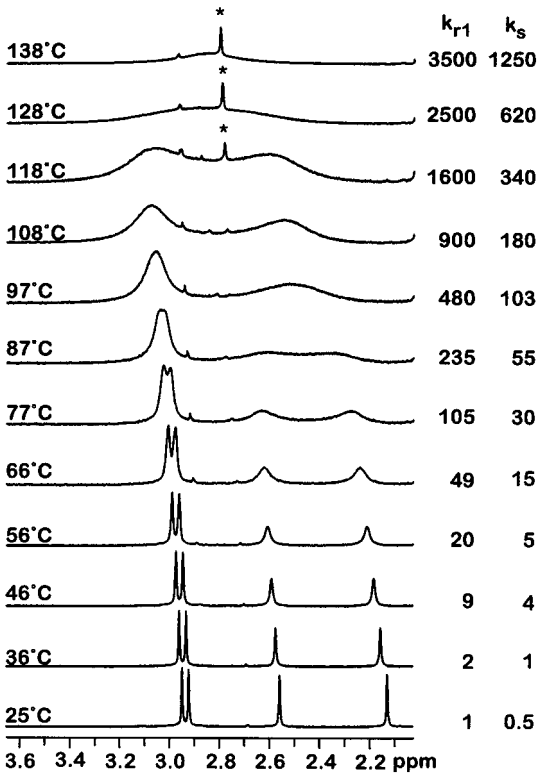


Figure 2. ^{1}H (400 MHz) variable temperature NMR spectra and associated rate constants for **2** in C_6D_5Br. Asterisk (*) denotes possible decomposition product.

inequivalent methyl groups are seen. The two upfield signals broaden, coalesce at 97 °C, and then begin to resharpen, corresponding to increased rate of rotation of the dithiocarbamate. Likewise, the two downfield peaks undergo a similar transformation with coalescence at about 87 °C, and this corresponds to exchange of the iminodithiolane methyls. At temperatures above 97 °C these two peaks broaden, coalesce, and begin to resharpen. This final process is the enantiomeric switching that exchanges the iminodithiolane and dithiocarbamate methyls. Rate constant for dithiocarbamate C−N rotation and enantiomeric switching are given in Figure 2, corresponding to $\Delta G^{\ddagger}$(25 °C) = 17.3 ± 0.3 and 17.9 ± 0.3 kcal/mol, respectively.[10]

(9) It was verified from other peaks that the symmetric and asymmetric broadening seen at higher temperatures was not due to any exchange process but rather field inhomogeneity resulting from difficulty in obtaining a good shim at these temperatures.

The complex pathways by which the labeled nuclei can exchange between the two enantiomers are shown in Figure 3. Line shape analysis indicates that the apparent line

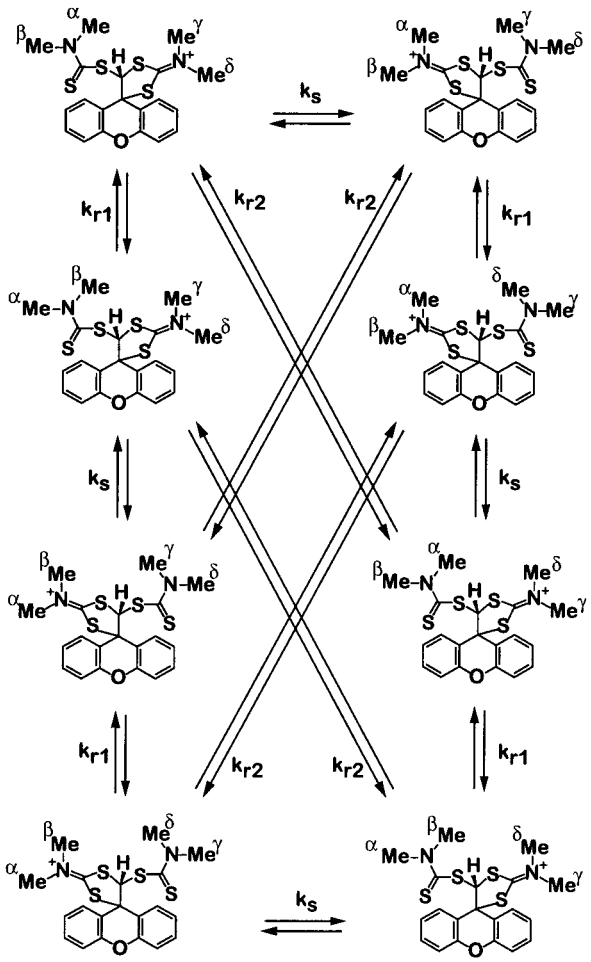


Figure 3. Mechanistic pathways that result in scrambling of labels (α, *β*, *γ*, and *δ*) to all four chemical environments. k_{r1} = rate constant for rotation about dithiocarbamate C−N bond, k_{r2} = rotation about iminodithiolane C═N bond, k_s = switching.

broadening and coalescence seen for the iminium methyls is not due to the direct C═N rotation[11] but rather to an indirect mechanism. Enantiomeric switching, followed by dithiocarbamate rotation, followed by reswitching (k_s, k_{r1}, k_s of Figure 3) results in an exchange that is identical to direct rotation about the iminium C═N (k_{r2} of Figure 3). While the coalescence of all four peaks to a single peak at high temperature is clear evidence for enantiomeric switching, the switching is also evident at much lower temperatures in the coalescence of the iminium methyls. This complexity provides a handle on the switching rate at lower temperatures.

(10) Similar barriers were seen in anisole-d_8 solvent (25 °C): $\Delta G_{r1}^{\ddagger}$ = 17.4 ± 0.3, $\Delta G_s^{\ddagger}$ = 18.4 ± 0.5.

(11) Line shape analysis was done with k_{r2} as a varied parameter. However, at low temperatures k_{r2} showed essentially no temperature dependence, whereas at high temperature the line shape is virtually unaffected by k_{r2} since the iminium line shape is dominated by the indirect mechanism.

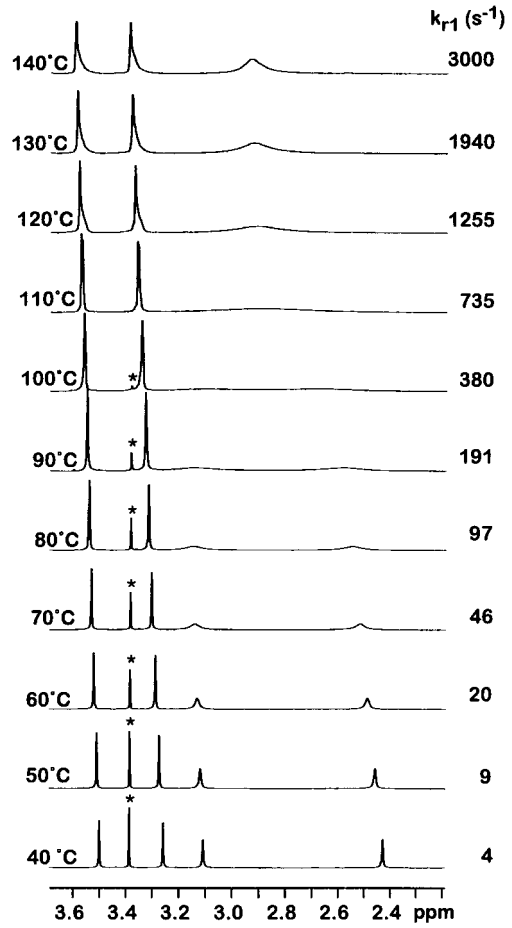


Figure 4. ^{1}H (400 MHz) variable temperature NMR and rate constants for **3** in anisole-d_8. Asterisk (*) denotes residual dioxane from sample preparation that diminishes in intensity as sample is warmed.

The 18.2 kcal/mol barrier for switching in **2** is slightly higher than the 16.5 kcal/mol barrier in the previously reported four-membered ring analogue, 4-dimethyldithiocarbamato-2-*N*,*N*-dimethylimino-1,3-dithietane.[12] The lower barrier for the latter may be due to release of ring strain in the dithietane intermediate or due to stabilization of a carbocation by two adjacent sulfur atoms.

These initial results were encouraging in that they demonstrate that interconversion of the iminodithiolane−dithiocarbamate functional groups can act as a switch. However, the thermal barrier is too low. Even at room temperature switching is fast enough to cause rapid racemization of enantiomers. Given the resonance stabilization and the tertiary nature of the inverting carbon, an S_N1 mechanism for the switching process is likely. This mechanism is supported by the lack of switching in **1**, where a carbocation intermediate would be disfavored because it is primary and lacks resonance stabilization. An S_N2 mechanism is plausible for **1**, but no switching is seen. If the mechanism is S_N1 for **2**, then the rate of switching ought to be substantially slowed with a fluorenyl substituent (**3**) since the intermediate would be an anti-aromatic 9-fluorenyl carbocation. The room temperature ^{1}H NMR of **3** in anisole-d_8 (Figure 4) again shows four distinct peaks in the methyl region. As temperature is increased the two upfield peaks from the *N*,*N*-dimethylcarbamate broaden, coalesce, and resharpen.[9] *Significantly, no other exchange broadening is seen, even in the iminium methyls, which would show switching at lower temperatures.* Thus fluorenyl substitution stops the switching process. Line shape analysis gave the rates listed in Figure 4 and $\Delta G^{\ddagger} = 17.5 \pm 0.1$ kcal/mol at 25 °C for internal rotation in the dithiocarbamate.

We have presented a general synthetic route for the preparation of Chiropticenes, whose switching is based on the degenerate intramolecular exchange of an iminodithiolane and a dithiocarbamate. Using molecular engineering we have shown that substituents at the 5 position influence the rate of switching by stabilizing the incipient prochiral cation. The electronic absorption maxima for **2** and **3** lie in the ultraviolet (λ_{max}(MeOH) $\approx$ 280 nm). Dithiocarbamates absorb in this region and are known to undergo photofragmentation.[13] Consequently, for optical activation, a chromophore that absorbs in the visible region will be required to avoid degradation resulting from high energy ultraviolet radiation. Modifications of these model systems employing extensively conjugated chromophores are in progress and will be reported in due course.

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Supporting Information Available: Full characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Schumaker, R. R.; Inoue, M.; Inoue, M. B.; Bruck, M. A.; Fernando, Q. *J. Chem. Soc., Chem. Comm.* **1991**, 719. The 5 kcal/mol barrier reported for the dithietane should be approximately 16.5 kcal/mol on the basis of the reported spectra, which show a separation of about 40 Hz and a coalescence temperature of about 60 °C ($k_C \approx 90$ s^{-1}).

(13) Kennard, K. C.; Van Allen, J. A. *J. Org. Chem.* **1959**, *24*, 470. Turner, S. R.; Blevins, R. W. *Macromolecules* **1990**, *23*, 1856.