Notes

Photoinduced 1,3-Proton Shift in Methyldithiepines as a Potential Way of Modulating Hyperpolarizabilities

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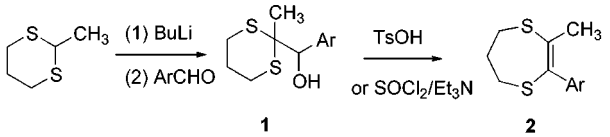
Reversible disruption of conjugation is a useful technique for affecting electronic properties of organic compounds. One can readily envision, for instance, a formal scheme involving a 1,3-H shift in a 1,2-propenylidene fragment connecting the donor (D) and acceptor (A) that is expected to exert a dramatic effect on properties such as UV−vis absorption, dipole moment, polarizability, and hyperpolarizability. Modulating the latter is a challenging problem, which may have far reaching implications for applied science. The known approaches vary from ultrafast optical modulation of quadratic nonlinearity from $Ru(bipy)_2$ complex in Langmuir−Blodgett assemblies[1] to pH control of NLO properties in hemicyanines and 4-amino-4′-nitrostilbenes.[2]

We have been exploring possibilities to use *photoinduced* proton shifts in allylic systems for altering electronic characteristics of molecules. Intramolecular proton transfer is widely used in tautomeric photochromes, and furthermore, its utilization for modulating NLO susceptibilities is certainly not unprecedented in the literature.[3] Our specific approach to this problem is based on a proton shift in the *all-carbon* allylic moiety of 2-methyl-3-aryl-6,7-dihydro-5*H*-[1,4]dithiepines (**2**), which we prepare from 2-methyl-1,3-dithiane and substituted benzaldehydes as follows:[4]



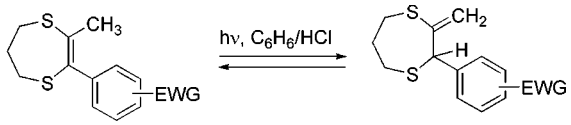
1 **2**

Ar = X-C_6H_4; X = (a) p-CN, (b) m-CN, (c) p-COOMe, (d) p-CHO, (e) H, (f) p-MeO

We now present an experimental mechanistic study of this novel 1,3-proton migration in a series of dithiepines **2**, augmented with ab initio evaluations of the second hyperpolarizability γ for **2** and how it is affected by its rearrangement into **3**.

Results and Discussion

We have found that upon irradiation in benzene containing small amounts of hydrochloric acid, dithiepines **2a**−**d** undergo 1,3-hydrogen migration leading to the desired conjugation disruption. The *exo*-methylenic dithiepanes **3a**−**d** are kinetic products and in the ground state they slowly rearrange back into the starting material. The dark back-reaction is accelerated in polar solvents.



2 **3**

Photolyses were carried out in degassed benzene solutions with a medium-pressure mercury lamp utilizing a Pyrex filter. Only dithiepines bearing an electron-withdrawing group (EWG) in the aromatic ring were reactive. Phenyl- or *p*-methoxyphenyl-substituted dithiepines **2e**,**f** degraded under these irradiation conditions. Other strong acids such as toluenesulfonic and trifluoroacetic also induced the rearrangement of **2**, whereas weaker acids, such as acetic, did not produce **3**. In addition, irradiation in benzene in the presence of a small amount of methanol with no acid added did not induce the 1,3-proton shift either.

To gain further experimental insight into the mechanism we carried out the irradiation of **2a** in benzene in the presence of a small amount of DCl/D_2O. The ^1H NMR spectrum of the reaction mixture showed considerable decrease (more than 50%) in the integration value of the benzylic proton in **3a**. We also synthesized a CD_3 derivative of **2a** (**2a-*d3***) and irradiated it in benzene in the presence of a small amount of hydrochloric acid. Only the benzylic peak grew in the proton NMR of reaction mixture. GC−MS corroborated these observations. The molecular ion peak for **2a** is 247. After irradiation in the presence of DCl, this value increased to 248 due to one deuterium atom incorporation. Likewise, the molecular ion peak for the deuterated

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(2) Shen, Y. R. In *Molecular nonlinear optics*; Zyss, J., Ed.: Academic Press: New York, 1994; p 113 and references therein.

(3) (a) Zhang, Y.; Lu, Z.-H. *Mater. Chem. Phys.* **2000**, *63*, 188. (b) Shiozaki, H.; Matsuoka, M. *THEOCHEM* **1998**, *427* 253. (c) Evans, C. C.; Bagieu-Beucher, M.; Masse, R.; Nicoud, J.-F. *Chem. Mater.* **1998**, *10*, 847. (d) Serrano, A.; Canuto, S. *Int. J. Quantum Chem.* **1998**, *70*, 745. (e) Shang, X.; Tang, G.; Zhang, G.; Liu, Y.; Chen, W.; Yang, B.; Zhang, X. *J. Opt. Soc. Am. B* **1998**, *15*, 854. (f) Houbrechts, S.; Clays, K.; Persoons, A.; Pikramenou, Z.; Lehn, J.-M. *Chem. Phys. Lett.* **1996**, *258*, 485. (g) Neykov, G.; Enchev, V.; Monev, V.; Kanev, I. *Mol. Eng.* **1995**, *5*, 347. (h) Albert, I. D. L.; Morley, J. O.; Pugh, D. *J. Phys. Chem.* **1995**, *99*, 8024. (i) Hoefer, T.; Kruck, P.; Kaiser, W. *Chem. Phys. Lett.* **1994**, *224*, 411.

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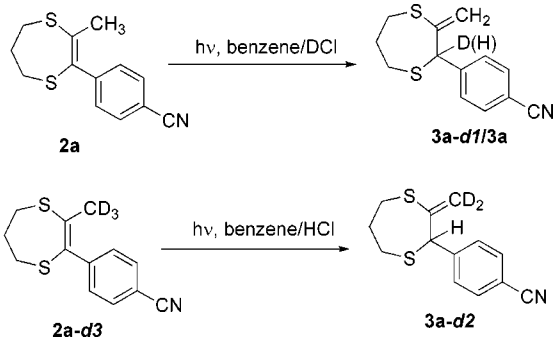
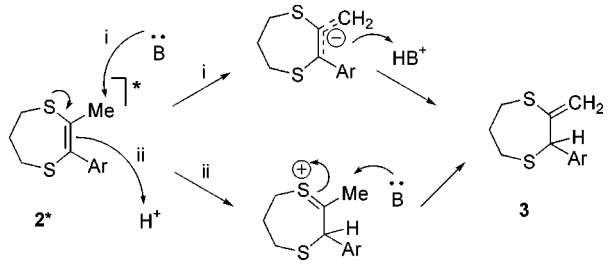
2a-*d3* is 250, and after irradiation the product's molecular ion was found to be 249 due to the one deuterium loss.

Running the photolysis under oxygen saturation conditions did not inhibit the 1,3-shift in **2a**,[5] ruling out the involvement of a triplet state.



Our experimental results indicate that the observed hydrogen migration is a nonconcerted proton transfer initiated in the excited singlet state of **2**. There are two possible mechanisms for such a proton migration, differing only in the order of C−H bond breaking/forming: (i) deprotonation of the methyl group in the excited state followed by reprotonation at the benzylic position or (ii) protonation of the benzylic position followed by deprotonation of the methyl.



The first mechanism is supported by the well-known fact that excited states are commonly much more acidic than their respective ground states. After deprotonation, the ground-state anion is reprotonated at the benzylic position. To better understand the regiochemistry of such kinetic protonations, we optimized the geometry of the anion derived from **2a** at the b3lyp/6-31g* level and analyzed the charge distribution utilizing Weinhold's natural bond orbital analysis.[6] The S−C−C−S fragment (Figure 1) of the anion is twisted heavily, with the two moieties—vinyl sulfide and aryl-CH—being almost orthogonal (CH_2−C−C−Ar dihedral angle is 90.7°). The cumulative natural charge of the vinyl sulfide fragment was calculated to be −0.05, whereas the S−CH−Ar moiety amassed the bulk of the negative charge, −0.73. It was therefore conceivable that the charge-controlled kinetic protonation of such anion would lead to **3a**, not back to **2a**.

The second mechanism, protonation-deprotonation, would necessitate accumulation of electronic density at the benzylic position of the excited **2**, implicating a charge-separated excited state. We note that due to the enhanced flexibility of the seven-member dithiepine ring, excited **2** may exist either in the form of a "conventional" TICT state (**A**) with the aromatic ring twisted out of conjugation, or the alternative (**B**), with a twisted S−C−C−S fragment. The state **B**, an *ionic* ethylenic state, is a good candidate for the benzylic protonation (path ii). Both states require an electron-withdrawing substitutent in the aromatic ring.

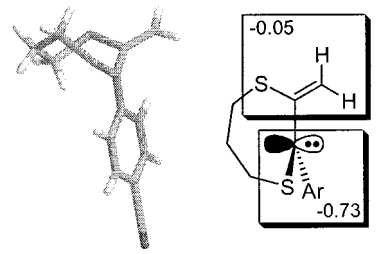


Figure 1. Deprotonated **2a**: ground-state b3lyp/6-31g* geometry (left) and the NBO charges breakdown for the twisted fragments (right).

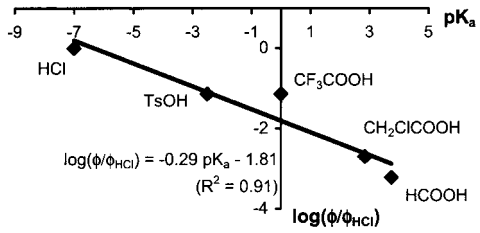
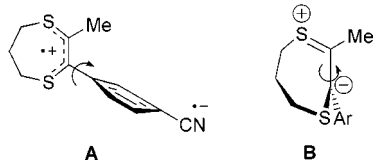


Figure 2. A Brønsted-type plot of the relative quantum efficiencies of the 1,3-shift in **2** as a function of pK_a.



Due to the size of the system, we were unable to computationally obtain the geometry and the charge distribution in the singlet excited state of **2a** at an adequate level of theory. However, we believe that the lack of reactivity in the absence of stronger acids supports path ii. If the path i were operational, with excited **2a** losing one of its methyl protons first, the generated ground-state anion should be able to deprotonate methanol or acetic acid; a very liberal lower estimate for pK_a of the benzylic proton in **3a** based on several analogous systems compiled in Bordwell's review[7] is 20.

As mentioned above, we observed no reaction in the presence of acetic acid (pK_a = 4.76). To cover a wider acidity range, we irradiated **2a** in the presence of formic (pK_a = 3.75) and chloroacetic (pK_a = 2.85) acids. In both cases, very small amounts of **3a** were observed after 2 h of irradiation. Although the acidity constants we used are reported for aqueous solutions, we found it informative to plot the logarithm of relative quantum efficiency of the rearrangement as a function of pK_a (a quasi-Brønsted plot). Figure 2 shows a relatively good fit with correlation coefficient exceeding 0.9 and the Brønsted's $\alpha = 0.29$, implicating general acid catalysis.

(5) although an increased amount of minor side products were observed, most certainly due to direct oxidation of sulfur.

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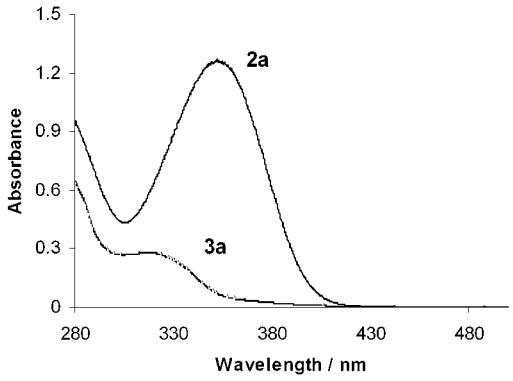

Figure 3. Comparison of the UV spectra for **2a** and **3a** in benzene.

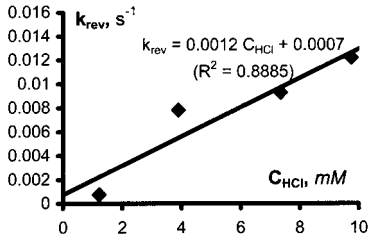

Figure 4. HCl concentration dependence of the rate of the reverse (dark) reaction **3a** → **2a** in acetonitrile.

There is no photoequilibration between **2a** and **3a**, possibly owing to considerable difference in their UV absorbance. While **2a** has a strong maximum at 350 nm, **3a** has only a weak absorbance above the Pyrex cutoff (Figure 3). The reverse reaction, which is also catalyzed by acids, occurs in the ground state. Most certainly it is a thermodynamically driven protonation−deprotonation. We optimized the geometries of **2a** and **3a** in the ground state at the b3lyp/6-31g* level and found that the zpe-corrected relative energy was about 7.5 kcal/mol (31.4 kJ/mol) favoring the starting **2a**.

Irradiation of **2a** in acetonitrile in the presence of HCl produces **3a**, which reverses to **2a** much faster than in nonpolar benzene. By photobleaching the UV absorbance at 350 nm and monitoring its recovery in the dark, we measured the rates of the reverse reaction. Figure 4 shows the dependence of the pseudo-first-order rate constant on the concentration of HCl: $k_{rev} = 0.0012C_{HCl}$. The intercept (0.0007) is very close to zero, indicating that a spontaneous (not catalyzed) back proton migration is virtually nonexistent. In the presence of 1 mM HCl (acetonitrile), $\tau_{1/2}$ is approximately 15 min. The proton NMR spectrum obtained after a full bleach-recovery cycle showed that only starting **2a** is present in the reaction mixture. At higher acid concentrations, the rate of the dark reaction was higher, but the absorbance never fully recovered to the starting value. We believe that this irreversible bleaching is due to hydrolysis of the dithiepane ring at higher acid concentrations.

Other nonpolar solvents, such as carbon tetrachloride, can also be successfully utilized in place of benzene to carry out this photoinduced 1,3-migration. As in benzene, the reverse reaction is much slower than in polar acetonitrile. An unexpected finding was that this rearrangement occurs in CCl_4 even with no acids added.

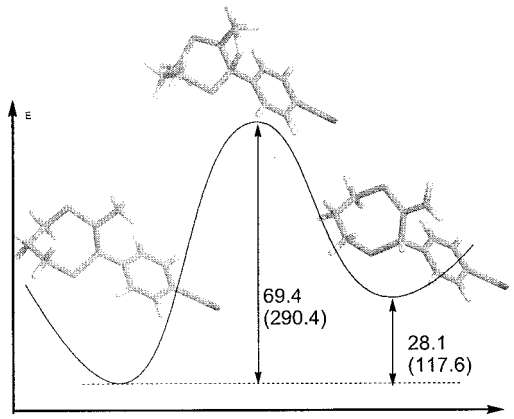

Figure 5. DFT energy diagram of **2**$^{\bullet+}$ → **TS** → **3**$^{\bullet+}$ transformation as a concerted 1,3-hydrogen shift. The relative energies are zpe-corrected: kcal/mol (kJ/mol).

We first considered the possibility that in acid-free carbon tetrachloride the mechanism may be different, e.g., involving a photoinduced single electron transfer, by analogy with our previous observations on CCl_4 photooxidation of aryldithiepines bearing electron donors in the aromatic ring.[4] It was then very tempting to explain the efficient **2**$^{\bullet+}$ → **3**$^{\bullet+}$ transformation in terms of a concerted 1,3-shift,[8] because of an apparent driving force, i.e., the necessity to shut off the conjugation of the electron-withdrawing aromatic ring from the sulfur-centered cation-radical.

To assess the feasibility of such a concerted 1,3-hydrogen migration in **2a**$^{\bullet+}$, we carried out DFT computations at the b3lyp/6-31g* level of theory on the cation-radical of the starting material (**2**$^{\bullet+}$), the cation-radical of the product (**3**$^{\bullet+}$), and the transition state. The geometries were optimized to stationary points as verified by vibrational analysis. Structures **2**$^{\bullet+}$ and **3**$^{\bullet+}$ showed no imaginary frequencies whereas the transition structure had one imaginary mode corresponding to the reaction coordinate. Zpe-corrected relative energies are presented in Figure 5.

First, our computations showed that **3a**$^{\bullet+}$ is actually *higher* in energy than **2a**$^{\bullet+}$ by 28.1 kcal/mol (117.6 kJ/mol). Notice that the conjugation interruption in **3a**$^{\bullet+}$ shuts off not only the electron-withdrawing aromatic ring but also the second sulfur atom, thus contributing to the overall destabilization of the cation radical. Most importantly, the activation barrier, 69.4 kcal/mol (290.4 kJ/mol), is prohibitively high for a concerted reaction to occur. We therefore believe that the reaction follows the same protonation-deprotonation mechanism with a trace amount of HCl either present in CCl_4, or generated during the photolysis. The maximum conversion in "acid-free" carbon tetrachloride is limited to about 50%, after which considerable degradation of products was observed. The reaction in benzene can be driven to near 100% conversion with very little degradation, allowing repetition of the cycle.

The photoinduced 1,3-proton migration in substituted dithiepines **2** may potentially be utilized for modulating hyperpolarizabilities. We addressed this issue theoreti-

(8) Concerted 1,3-hydrogen migrations in cation radicals were reported previously. See, for example: Nguen, M. T.; Landuyt, L. Vanquickenborne L. G. *Chem. Phys. Lett.* **1991**, *182*, 225 and references therein.

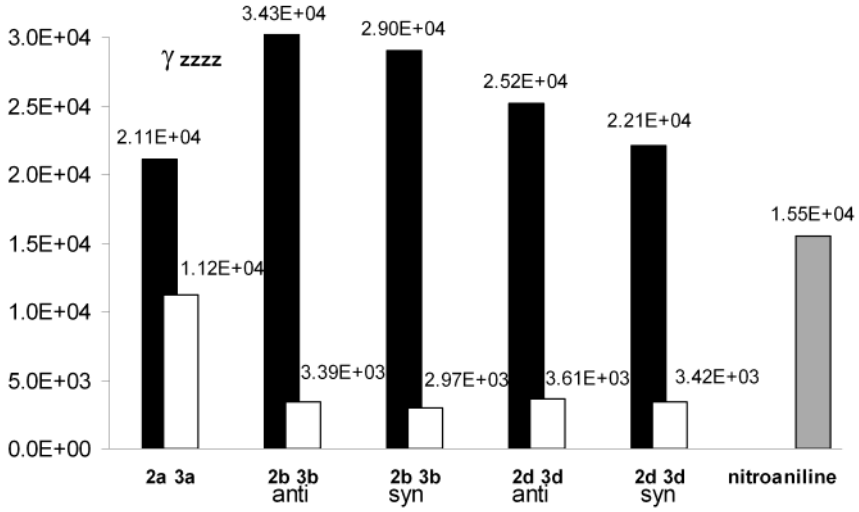

Figure 6. Second hyperpolarizabilities in the "on" (**2a,b,d**) and "off" (**3a,b,d**) states as compared with that of nitroaniline. γ_{zzzz} values for compounds **2b** and **3b** are computed for both syn and anti (with respect to the methyl) conformations of 3-cyanophenyl group; the same applies to the formyl's oxygen in compounds **2d** and **3d**.

cally by carrying out the finite field computations at rhf level of theory utilizing 3-21g* basis set and comparing our calculated values for second hyperpolarizability with that calculated by Dupuis for one of the organic NLO standards, *p*-nitroaniline.[9] As we expected, the value for the axial component of the second hyperpolarizability γ, γ_{zzzz} calculated for **2a**,**b**,**d** was impressively high, ranging from 2×10^4 to 3×10^4 atomic units (Figure 6). This value decreased dramatically in the "off" states **3**, because of disrupted conjugation between the donor, dithiepine ring, and the aryl acceptor. As a comparison, the value of γ_{zzzz} calculated by Dupuis for *p*-nitroaniline is 1.55×10^4. The second hyperpolarizability for **2b** (largest computed in our series) exceeded it by a factor of 2. At the same time, it drops by an order of magnitude in the "off" state (**3b**), amounting only to about 20% of the nitroaniline's value. Compounds **2a**,**d** showed similar large changes in γ_{zzzz}, see Figure 6.

To summarize, we have developed a novel methyldithiepine-based photochromic system, capable of a reversible photoinduced 1,3-proton shift, which effectively disrupts the conjugation between the donor and the acceptor moieties, offering among other things a potential way of modulating hyperpolarizabilities. Our mechanistic rationale includes protonation of the ethylenic moiety in the excited dithiepine **2** followed by the ground-state deprotonation of the methyl leading to **3**. The reverse dark reaction, which takes place in the ground state, is also a protonation−deprotonation process. It is accelerated by solvent polarity and acidity of the media.

Experimental Section

General Methods. Unless otherwise specified, solvents and reagents were purchased from commercial suppliers and used without further purification. THF was refluxed over and distilled from potassium benzophenone ketyl prior to use. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Varian Mercury 400 MHz instrument. In $CDCl_3$, TMS was used as an internal standard; in C_6D_6, benzene is used as an internal standard. UV−vis spectra were obtained by using DU Series 600 Spectrophotometer (Beckman Instruments, Inc.). Column chromatography was performed on silica gel, 70−230 mesh ASTM, using ethyl acetate−hexane mixtures as eluent. HP 6890 with MSD detector was used to analyze the reaction mixtures. The Pyrex-filtered output of a medium-pressure Hanovia lamp was utilized as the UV source.

Computational Methods. Ab initio geometry optimizations were carried out with the Gaussian 98 package[10] using density functional theory (DFT) at the b3lyp/6-31g* level (the Becke three-parameter hybrid functional combined with Lee, Yang, and Parr correlation functional[11]). The stationary points were characterized with vibrational analysis at the same level of theory. Zero-point energies were scaled by 0.9804.[12] The reported values for the second hyperpolarizability were obtained utilizing the finite field approach (field increments −0.002, −0.001, 0.001, and 0.002) as implemented in GAMESS ab initio package.[13]

Synthesis of Deuterated 2-Methyl-d_3-[1,3]dithiane. A solution of 1,3-dithiane (4.23 g, 35.2 mmol) in 100 mL of freshly distilled THF was cooled to −25 °C under nitrogen. Then *n*-butyllithium (1.6M solution in hexanes, 42.3 mmol, 26.0 mL) was added dropwise upon stirring. The mixture was stirred for 2 h at −25 °C before the temperature was lowered to −78 °C. Iodomethane-d_3 (5.00 g, 35.2 mmol) was added dropwise into this solution of anion upon stirring. After 1 h at this temperature and then 2 h at −25 °C, the reaction was quenched with saturated solution of ammonium chloride, extracted twice with 50 mL of diethyl ether, and dried over magnesium sulfate. The solvent was then removed and the residue was distilled at reduced pressure 67−68 °C/4 mmHg to give 3.62 g yellowish oil, 75% yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.11 (s, 1H), 2.95−2.77 (m, 4H), 2.15−2.05 (m, 1H), 1.88−1.76 (m, 1H).

General Procedure for the Methyldithiane−Aldehyde Adduct Preparation. A solution of 2-methyl-1,3-dithiane (1.04

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g, 7.76 mmol) in 50 mL of freshly distilled THF was cooled to −25 °C under nitrogen. Then *n*-butyllithium (1.6 M solution in hexanes, 8.5 mmol, 5.3 mL) was added dropwise upon stirring. The resulting mixture was stirred for 2 h at −25 °C. The solution of the dithianyl anion was added dropwise to a vigorously stirred solution of an appropriate aromatic aldehyde[14] (7.76 mmol) in 20 mL of THF at −78 °C. The reaction mixture was stirred for 1 h at this temperature and then stored in a freezer at −25 °C overnight. The subsequent aqueous workup included quenching the reaction mixture with a saturated solution of ammonium chloride, extracting twice with 30 mL of diethyl ether, and drying the combined organic extracts over magnesium sulfate. The solvent was then removed in a vacuum, and the residue was purified on a slurry-packed silica gel column, eluted with ethyl acetate/hexane.

4-[Hydroxy(2-methyl[1,3]dithian-2-yl)methyl]benzonitrile (1a): 67%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63−7.57 (m, 4H), 5.12 (s, 1H), 3.40 (s, 1H), 3.23−3.16 (m, 1H), 3.11−3.04 (m, 1H), 2.77−2.66 (m, 2H), 2.23−2.15 (m, 1H), 1.98−1.85 (m, 1H), 1.210-(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.9, 130.7, 129.1, 118.7, 112.4, 72.6, 53.5, 26.7, 26.0, 24.0, 22.0. Anal. Calcd for $C_{13}H_{15}S_2$-ON: C, 58.82; H, 5.70. Found: C, 58.42; H, 5.77.

4-[Hydroxy(2-methyl-*d*$_3$-[1,3]dithian-2-yl)methyl]benzonitrile (1a-*d*$_3$). 2-Methyl-d_3-[1,3]dithiane was used instead of 2-methyl[1,3]dithiane: 57%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59−7.61(m, 4H), 5.13 (s, 1H), 3.39 (s, 1H), 3.24−3.16 (m, 1H), 3.12−3.03 (m, 1H), 2.78−2.65 (m, 2H), 2.24−2.15 (m, 1H), 1.97−1.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.9, 130.7, 129.1, 118.7, 111.5, 72.6, 53.3, 26.7, 26.0, 24.0.

3-[Hydroxy(2-methyl[1,3]dithian-2-yl)methyl]benzonitrile (1b): 76%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (s, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.42 (t, J = 8 Hz, 1H) 5.11 (s, 1H), 3.39 (s, 1H), 3.25−3.16 (m, 1H), 3.15−3.05 (m, 1H), 2.80−2.66 (m, 2H), 2.26−2.10 (m, 1H), 1.99−1.86 (m, 1H), 1.20(s, 3H).

4-[Hydroxy(2-methyl[1,3]dithian-2-yl)methyl]benzoic acid methyl ester (1c): 47%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.976 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 5.13 (s, 1H), 3.90 (s, 3H), 3.38 (s, 1H), 3.24−3.15 (m, 1H), 3.10−3.01 (m, 1H), 2.76−2.64 (m, 2H), 2.21−2.12 (m, 1H), 1.96−1.85 (m, 1H), 1.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.6, 142.6, 129.4, 128.4, 128.3, 73.1, 53.7, 52.0, 26.7, 26.0, 24.1, 22.3. Anal. Calcd for $C_{14}H_{18}S_2O_3$: C, 56.35; H, 6.08. Found: C, 56.49; H, 6.15.

(4-Methoxyphenyl)(2-methyl[1,3]dithian-2-yl)methanol (1f): 86%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 5.05 (s, 1H), 3.795 (s, 3H), 3.21 (s, 1H), 3.22−3.13 (m, 1H), 3.10−3.01 (m, 1H), 2.76−2.63 (m, 2H), 2.18−2.09 (m, 1H), 1.96−1.84 (m, 1H), 1.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.0, 129.3, 112.6, 73.6, 55.2, 54.1, 26.7, 26.0, 24.4, 22.4. Anal. Calcd for $C_{13}H_{18}S_2O_2$: C, 57.74; H, 6.71. Found: C, 57.82; H, 6.76.

General Procedure for Preparation of the Dithiepines 2. Method A. A solution of methyldithiane−aldehyde adduct (1 mmol) and triethylamine (5 mmol) in 20 mL of CCl_4 was cooled to 0 °C, and $SOCl_2$ (1.7 mmol) was added upon stirring. After 2 min, the reaction was quenched with the addition of 10 mL of aqueous HCl. The organic phase was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic phase was dried with $MgSO_4$, concentrated in a vacuum, and purified on a slurry-packed silica gel column and eluted with ethyl acetate/hexane. **Method B.** To a refluxed solution of methyldithiane-carbonyl adduct (1 mmol) in benzene (10 mL) under nitrogen atmosphere was added TsOH·H_2O (0.1 mmol) and the mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature and washed with saturated $NaHCO_3$ (10 mL). The aqueous layer was extracted with benzene (10 mL × 2). The organic phases were combined, dried with $MgSO_4$, and concentrated in a vacuum. The residue was purified on a slurry-packed silica gel column and eluted with ethyl acetate/hexane.

(14) Compound **2d** was synthesized starting with the monodiethyl acetal of terephthalic aldehyde. Under the conditions of acid-catalyzed dehydrative ring expansion (**1d-monoacetal** → **2d**), the acetal protection was also removed regenerating free formyl in the para-position of **2d**. We introduced the acetal into the second step without additional purification.

4-(3-Methyl-6,7-dihydro-5*H*-[1,4]dithiepin-2-yl)benzonitrile (2a): method B; 71%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.59 (d, J = 7.8 Hz, 2H), 7.38 (d, J = 7.8 Hz, 2H), 3.56 (t, J = 5.6 Hz, 2H), 3.52 (t, J = 5.6 Hz, 2H), 2.14 (quintet, J = 5.6 Hz, 2H), 1.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 131.9, 130.5, 129.8, 126.8, 118.6, 110.9, 33.1, 31.4, 29.6, 24.5; MS (EI) *m*/*z* (relative intensity) 247 (M^+, 100), 218 (10), 173 (20), 140 (15), 106 (20). Anal. Calcd for $C_{13}H_{13}S_2N$: C, 63.12; H, 5.30. Found: C, 62.75; H, 5.40.

4-(3-Methyl-*d*$_3$-6,7-dihydro-5*H*-[1,4]dithiepin-2-yl)benzonitrile (2a-*d*$_3$): method B; 70%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.59 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 3.56 (t, J = 6.0 Hz, 2H), 3.52 (t, J = 6.0 Hz, 2H), 2.14 (quintet, J = 6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 131.9, 130.5, 129.8, 126.8, 118.6, 110.9, 33.1, 31.4, 29.7; MS (EI) *m*/*z* (relative intensity) 250 (M^+, 100), 221 (10), 176 (35), 146 (30), 106 (85).

3-(3-Methyl-6,7-dihydro-5*H*-[1,4]dithiepin-2-yl)benzonitrile (2b): method B; 79%; ^{1}H NMR ($CDCl_3$), 400 MHz) δ 7.58 (s,1H), 7.54−7.47 (m, 2H), 7.40 (t, J = 7.6 Hz, 1H), 3.59−3.50 (m, 4H), 2.14 (quintet, J = 5.8 Hz, 2H), 1.61 (s, 3H); MS (EI) *m*/*z* (relative intensity) 247 (M^+, 100), 218 (10), 173 (25), 140 (30), 106 (90), 73 (60). Anal. Calcd for $C_{13}H_{13}S_2N$: C, 63.12; H, 5.30. Found: C, 63.31; H, 5.49.

4-(3-Methyl-6,7-dihydro-5*H*-[1,4]dithiepin-2-yl)benzoic acid methyl ester (2c): method A; 44%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 9.0 Hz, 2H), 7.34 (d, J = 9.0 Hz, 2H), 3.91 (s, 3H), 3.55 (t, J = 5.6 Hz, 2H), 3.52 (t, J = 5.6 Hz, 2H), 2.14 (quintet, J = 5.6 Hz, 2H), 1.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.6, 146.1, 129.7, 129.4, 128.9, 128.7, 127.8, 55.2, 33.0, 31.5, 29.8, 24.6; MS (EI) *m*/*z* (relative intensity) 280 (M^+, 50), 206 (20), 175 (22), 143 (25), 115 (40), 106 (100), 73 (98), 59 (65). Anal. Calcd for $C_{14}H_{16}S_2O_2$: C, 59.97; H, 5.75. Found: C, 60.37; H, 6.04.

4-(3-Methyl-6,7-dihydro-5*H*-[1,4]dithiepin-2-yl)benzaldehyde (2d). Deprotection of the *p*-formyl group and dehydrative ring expansion in the diethyl acetal of **1d** were performed in one step using 1 equiv of TsOH·H_2O: 65%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.98 (s,1H), 7.82 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 3.58−3.50 (m, 4H), 2.15 (quintet, J = 5.8, 2H), 1.75 (s, 3H); MS (EI) *m*/*z* (relative intensity) 250 (M^+, 100), 221 (10), 176 (12), 147 (15), 106 (60), 89 (10).

2-(4-Methoxyphenyl)-3-methyl-6,7-dihydro-5*H*-[1,4]dithiepine (2f): method A; 31%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 3.50 (t, J = 5.6 Hz, 2H), 3.48 (t, J = 5.6 Hz, 2H), 2.09 (quintet, J = 5.6 Hz, 2H), 1.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.6, 133.5, 130.8, 128.7, 126.0, 113.4, 55.2, 32.7, 31.4, 29.7, 24.5; MS (EI) *m*/*z* (relative intensity) 252 (M^+, 100), 178 (40), 163 (40), 151 (35), 146 (75), 131 (35), 103 (40), 77 (38). Anal. Calcd for $C_{13}H_{18}S_2O_2$: C, 61.86; H, 6.39. Found: C, 62.12; H, 6.58.

General Photochemical Procedure. The solution of an appropriate methyldithiepine (5 mg) in 0.6 mL of CCl_4 was degassed by four freeze−pump−thaw cycles and sealed in a Pyrex NMR tube. The irradiations were carried out in a carousel Rayonet photoreactor. The sample was analyzed by NMR immediately after the irradiation. In an alternative method, an appropriate methyldithiepine (5 mg) was dissolved in 0.6 mL of benzene-d_6 containing 1 μL of concentrated aqueous HCl in a Pyrex NMR tube. It was degassed, irradiated, and analyzed as described above. Most of the acid and minor side products can be removed by filtering the solution through a small pipet packed with basic aluminum oxide.

4-(3-Methylene[1,4]dithiepan-2-yl)benzonitrile (3a): ^{1}H NMR (C_6D_6, 400 MHz) δ 7.09 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 5.34 (s, 1H), 4.57 (s, 1H), 4.56 (s, 1H), 2.59−2.45 (m, 2H), 2.40−2.29 (m, 2H), 1.64−1.51(m, 2H); ^{13}C NMR (C_6D_6, 100 MHz) δ 145.9, 144.8, 132.0, 129.3, 118.7, 118.5, 111.8,55.6, 33.6, 32.4, 30.4; MS (EI) *m*/*z* (relative intensity) 247 (M^+, 20), 172 (10), 140 (15), 106 (100).

3-(3-Methylene[1,4]dithiepan-2-yl)benzonitrile (3b): ^{1}H (C_6D_6, 400 MHz) δ 7.47 (s,1H), 7.33 (d, J = 7.3 Hz,1H), 6.88 (d, J = 7.3 Hz, 1H), 6.65 (t, J = 8.0 Hz, 1H), 5.32 (s, 1H), 4.56 (s, 1H), 4.54 (s, 1H), 2.59−2.52 (m, 2H), 2.39−2.29 (m, 2H), 1.63−1.50 (m, 2H).

4-(3-Methylene[1,4]dithiepan-2-yl)benzoic acid methyl ester (3c) :^{1}H NMR (C_6D_6, 400 MHz) δ 8.08 (d, J = 8.4 Hz, 2H),

7.43 (d, J = 8.4 Hz, 2H), 5.38 (s, 1H), 4.757 (s, 1H), 4.71 (s, 1H), 4.48 (s, 3H), 2.69−2.56 (m, 2H), 2.51−2.35 (m, 2H), 1.66−1.55 (m, 2H); ^{13}C NMR (C_6D_6, 100 MHz) δ 166.4, 146.5, 145.3, 130.6,129.0, 127.4, 117.9, 55.9, 51.8, 33.7, 32.0, 30.5; MS (EI) m/z (relative intensity) 280 (M^+, 10), 143 (13), 115 (15), 106 (100), 59 (10).

4-(3-Methylene[1,4]dithiepan-2-yl)benzaldehyde (3d): ^{1}H (C_6D_6, 400 MHz) δ 9.62 (s, 1H), 7.49 (d, J = 7.9 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 5.39 (s, 1H), 4.72 (s, 1H), 4.69 (s, 1H), 2.68−2.55 (m, 2H), 2.53−2.36 (m, 2H), 1.60−1.48 (m, 2H).

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Supporting Information Available: NMR spectra and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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