Tetrathiafulvalenenaphthalenophanes: Planar Chirality and *cis/trans* Photoisomerization

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A cyclophane incorporating one 1,5-dioxynaphthalene ring system and one tetrathiafulvalene (TTF) unit bridged by [SCH_2CH_2O] linkages has been synthesized. In this cyclophane, the TTF unit can adopt either *cis* or *trans* configurations. In addition, the 1,5-dioxynaphthalene ring system imposes one element of planar chirality on this cyclophane. A second element of planar chirality is introduced by the *trans* form of the TTF unit. Thus, the cyclophane exists in diastereoisomeric forms as three pairs of enantiomers. The enantiomeric pairs associated with the *cis* form of the TTF unit, as well as one of those associated with the *trans* form, have been isolated by crystallization, and their structures assigned in the solid state by single-crystal X-ray analyses. In solution, *cis*/*trans* isomerization occurs when either the *cis* or the *trans* form of the cyclophane is exposed to light. The photoisomerization reaction can be followed by ^{1}H NMR and UV−vis spectroscopies, as well as by HPLC. The photoisomerization quantum yield has been measured at two different excitation wavelengths (406 and 313 nm). In both cases, the *trans* → *cis* process ($\Phi = 0.20$ at 406 nm) is much more efficient than the reverse *cis* → *trans* process ($\Phi = 0.030$ at 406 nm). Since the absorption spectra of the *trans* and *cis* isomers are different and the quantum yield of the *trans* → *cis* photoisomerization reaction depends on the excitation wavelength, the mole fraction of the two diastereoisomers present at the photostationary state depends on the wavelength of the exciting light. No isomerization occurs when the solutions, regardless of the mole fraction of the two diastereoisomers, are stored in the dark.

Introduction

Molecular and supramolecular systems incorporating one or more tetrathiafulvalene (TTF) units are attracting increasing attention[1] as a result of the redox, electron-donating, and structural properties of TTF. Indeed, TTF can be oxidized reversibly to its radical monocation $TTF^{\bullet +}$, which in turn can be oxidized reversibly to its dication TTF^{2+}. Furthermore, TTF forms donor/acceptor complexes in solution and in the solid state with a variety of acceptors. In appropriate bis-, tris-, and tetrasubstituted TTF derivatives, the [C═C] double bond linking the two five-membered rings can adopt *cis* or *trans* configurations. The *cis*/*trans* isomerization of some of these TTF derivatives can be controlled chemically,[2] electrochemically,[3] or photochemically,[4] thus offering the possibility of generating molecular-sized switches.[5] To gain further insight into the factors governing the *cis*/*trans* isomerization, we synthesized a small and rigid cyclophane incorporating a TTF unit bridged by [SCH_2CH_2O] linkages to a 1,5-dioxynaphthalene ring system. The incorporation of the 1,5-dioxynaphthalene ring system imposes one element of planar chirality into the cyclophane molecules. Furthermore, the *trans* form of TTF introduces a second element of planar chirality. Hence, a total of three possible pairs of enantiomers are associated with the three diastereoisomeric forms of this cyclophane. Here, we report (i) the synthesis and separation of two of the diastereoisomeric forms of this cyclophane, (ii) the solid-state structures of these diastereoisomers, and (iii) the results of a quantitative investigation of the photoisomerization reactions exhibited by the *cis* and *trans* forms.

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(1) For TTF-containing molecular and supramolecular systems, see: (a) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355−390. (b) Jørgensen, T.; Hansen, T. K.; Becher, J. *Chem. Soc. Rev.* **1994**, *23*, 41−51. (c) Nielsen, M. B.; Becher, J. *Liebigs Ann./Recl.* **1997**, 2177−2187. (d) Becher, J.; Li, Z. T.; Blanchard, P.; Svenstrup, N.; Lau, J.; Nielsen, M. B.; Leriche, P. *Pure Appl. Chem.* **1997**, *69*, 465−470. (e) Bryce, M. R.; Devonport, W.; Goldenberg, L. M.; Wang, C. *Chem. Commun.* **1998**, 945−951. (f) Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11−23.

(2) For an example of acid-induced *cis*/*trans* isomerization of a TTF derivative, see: Souizi, A.; Robert, A. *J. Org. Chem.* **1987**, *52*, 1610−1611.

(3) For examples of *cis*/*trans* isomerizations of TTF derivatives induced electrochemically, see: (a) Boubekeur, K.; Lenoir, C.; Batail, P.; Carlier, R.; Tallec, A.; Le Paillard, M.-P.; Lorcy, D.; Robert, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1379−1381. (b) Lau, J.; Blanchard, P.; Riou, A.; Jubault, M.; Cava, M. P.; Becher, J. *J. Org. Chem.* **1997**, *62*, 4936−4942.

(4) For an example of light-induced *cis*/*trans* isomerization of a TTF derivative, see: Kreitsberga, Y. N.; Liepin'sh, É. É.; Mazheika, I. B.; Neilands, O. Y. *Zh. Org. Khim.* **1986**, *22*, 416−420.

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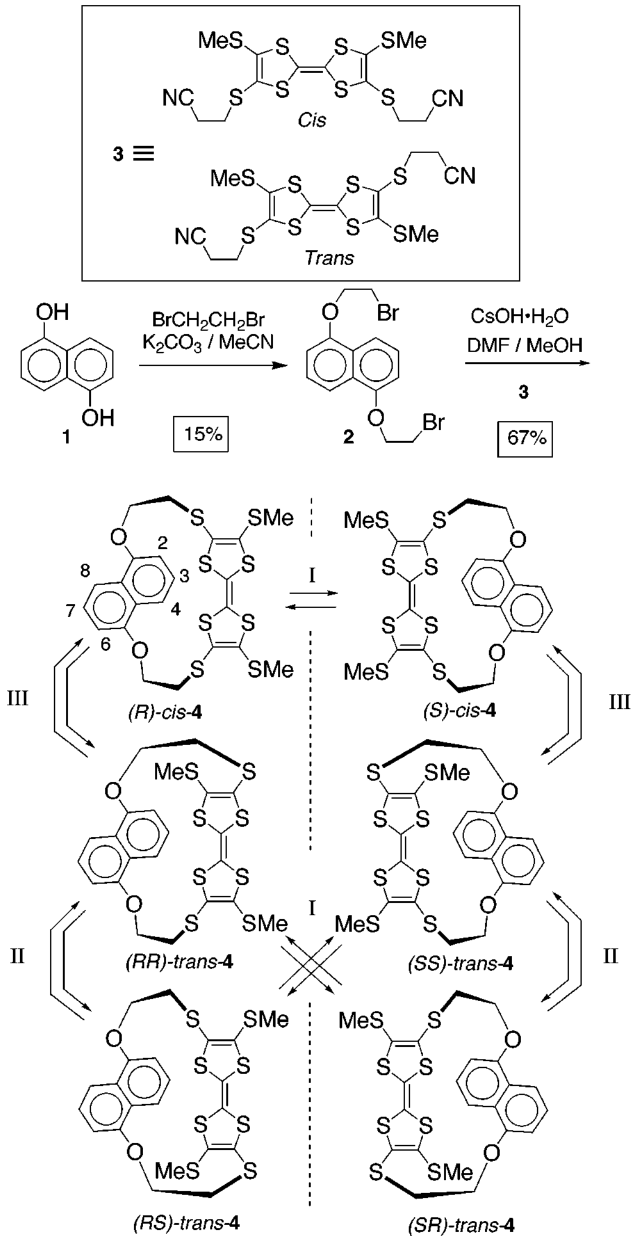

Figure 1. The synthesis of cyclophane **4** [note that (*RS*/*SR*)-*trans*-**4** is not formed] and the dynamic processes (I–III) responsible for the interconversions between the three diastereoisomers of **4** and the inversion between the three pairs of enantiomers.

Results and Discussion

Synthesis and Stereochemistry. 1,5-Dihydroxynaphthalene (**1**) was alkylated (Figure 1) with 1,2-dibromoethane to afford the dibromide **2** in a yield of 15%. High-dilution reaction of **2** with a bisthiolate produced in situ by treating **3** with 2.2 equiv of CsOH•H$_2$O gave compounds that were subsequently shown to be a mixture of the *cis* and *trans* isomers of the cyclophane **4**, in an overall yield of 67%.

In the cyclophane **4**, the TTF unit can adopt (Figure 1) either a *cis* or a *trans* configuration. A pair of enantiomers, an *(R/S)* modification, are associated with the *cis* form of **4** since it incorporates one element of planar chirality, namely, the 1,5-dioxynaphthalene ring system. By contrast, two pairs of enantiomers, *(RR/SS)* and *(RS/SR)*, are associated with the *trans* form of **4**, which possesses two elements of planar chirality, namely, the 1,5-dioxynaphthalene ring system and the *trans*-TTF unit. The inversion between the two enantiomers of *cis*-**4** has to involve a 180° rotation (Process I) of the 1,5-dioxynaphthalene ring system about its [O···O] axis, while the inversion between those of *trans*-**4** can only occur as a result of Process I and a 180° rotation (Process II) of the TTF unit about its [MeS···SMe] axis. The *cis/trans* isomerization (Process III) of the TTF unit can interconvert *cis*-**4** into *trans*-**4**. Finally, the interconversion of the two diastereoisomers with the *trans* configuration can be achieved in principle by either Process I or Process II.

High-Performance Liquid Chromatography. High-performance liquid chromatographic (HPLC) analysis of CH$_2$Cl$_2$ solutions of **4** as a mixture of compounds revealed peaks at retention times of 14.7 and 15.5 min, indicating the presence of two diastereoisomers, which were subsequently shown by ^{1}H NMR spectroscopy to be *(R/S)-cis*-**4** and *(RR/SS)-trans*-**4**, respectively. The same retention times were observed when CH$_2$Cl$_2$ solutions of the pure isomers *(R/S)-cis*-**4** and *(RR/SS)-trans*-**4**, previously isolated upon crystallization and characterized by X-ray crystallography (vide infra), were analyzed under otherwise identical conditions. Given the availability of the pure *cis* and *trans* isomers, the light-induced *cis/trans* isomerization of the TTF unit could be followed by HPLC. A CHCl$_3$ solution of *(R/S)-cis*-**4** was exposed to ambient light and analyzed periodically by HPLC. At equilibrium (photostationary state), a *cis/trans* ratio of ca. 1.5 was estimated.

X-ray Crystallography. In one instance, crystallization of the cyclophane **4** from a mixture of CH$_2$Cl$_2$/hexane afforded small orange hexagonal cross-section needles. X-ray crystallographic analysis of these needles revealed (Figure 2) them to contain the *(R/S)-cis*-**4** isomer. The [C–S] distances are in the range 1.746(5)–1.772(6) Å. The [C═C] double bonds in the two five-membered rings are of length 1.318 and 1.330(8) Å, while the [C═C] double bond linking the two rings is 1.340(7) Å. Both rings are folded about their [S···S] vectors, though the folding is asymmetric, being 6° in one ring and 23° in the other. The 1,5-dioxynaphthalene ring system is tilted by 22° and displaced with respect to the plane defined by the four sulfur atoms of the TTF unit. The shortest distance of the sulfur atom that overlaps partially the 1,5-dioxynaphthalene ring system from its plane is >4 Å. Inspection of the packing of the molecules revealed (Figure 3) an S_6 symmetric motif, wherein the six

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(5) For reviews, see: (a) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, 1991. (b) Balzani, V. *Tetrahedron* **1992**, *48*, 10443–10514. (c) Bissell, R. A.; de Silva, A. P.; Gunaratne, H. Q. N.; Lynch, P. L. M.; Maguire, G. E. M.; McCoy, C. P.; Sandanayake, K. R. A. S. *Top. Curr. Chem.* **1993**, *168*, 223–264. (d) De Silva, A. P.; McCoy, C. P. *Chem. Ind.* **1994**, 992–996. (e) Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, *24*, 197–202. (f) Benniston, A. C. *Chem. Soc. Rev.* **1996**, *25*, 427–435. (g) Shinkai, S. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.;Pergamon: Oxford, 1996; Vol. 1, pp 671–700. (h) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1566. (i) Ward, M. D. *Chem. Ind.* **1997**, 640–645. (j) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71–80. (k) Boulas, P. L.; Gómez-Kaifer, M.; Echegoyen, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 216–247. (l) Balzani, V.; Gómez-López, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405–414. (m) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611–619. (n) Niemz, A.; Rotello, V. M. *Acc. Chem. Res.* **1999**, *32*, 42–52. (o) Kaifer, A. E. *Acc. Chem. Res.* **1999**, *32*, 62–71. (p) Fabbrizzi, L.; Licchelli, M.; Pallavicini P. *Acc. Chem. Res.* **1999**, *32*, 846–853.

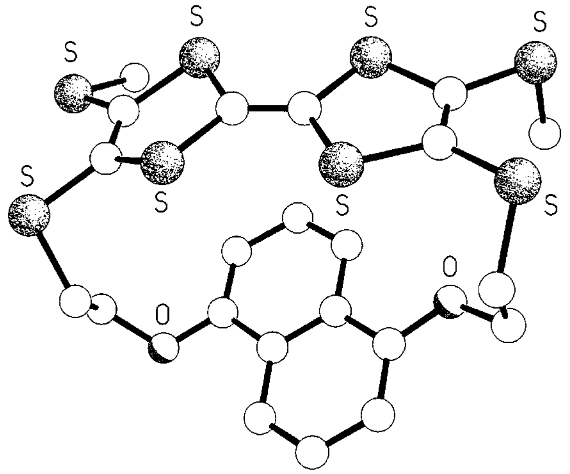

Figure 2. Ball-and-stick representation of the geometry adopted by *(R)-cis*-**4** in the solid state.

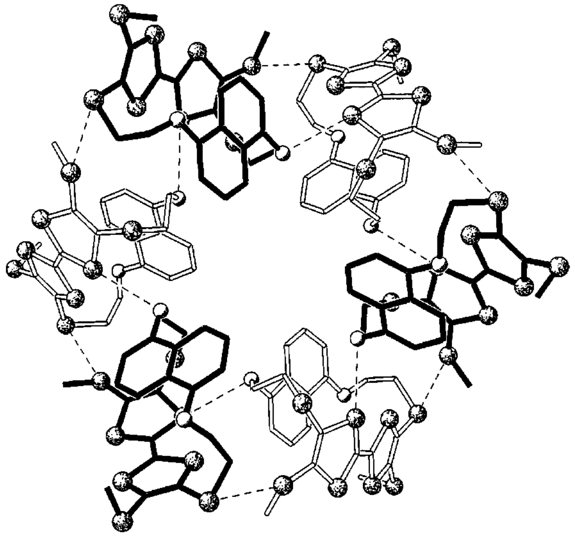

Figure 3. One of the S_6 symmetric motifs formed by *(R/S)-cis*-**4** in the solid state.

molecules are linked via pairs of [S···O] and [S···S] electrostatic interactions of length 3.23 and 3.55 Å, respectively.[6] Molecules adjacent to those in this motif have one of their five-membered rings π-stacked with their centrosymmetrically related neighbors, the mean interplanar separation being 3.44 Å.

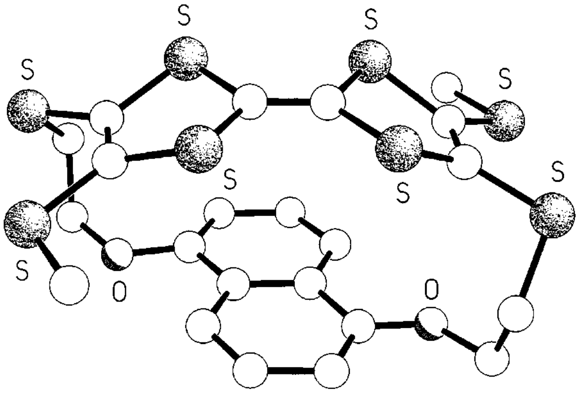

Figure 4. Ball-and-stick representation of the geometry adopted by *(RR)-trans*-**4** in the solid state.

X-ray crystallographic analysis of another set of crystals, grown from the cyclophane **4** dissolved in the same mixture of solvents but having a distinctly different crystal morphology (blocky yellow rhombs), showed (Figure 4) them to contain the *(RR/SS)-trans*-**4** isomer. The molecule has approximate noncrystallographic C_2 symmetry about an axis passing through the bond linking two five-membered rings and the center of the 1,5-dioxynaphthalene ring system. There is no significant torsional twist (<1°) about the [C=C] double bond linking the two five-membered rings, both of which have folded conformations (out of plane fold angles of 28° and 29°, about their respective [S···S] vectors). The pattern of bonding within each of these rings is essentially the same, with [C−S] bonds in the range 1.745(5)−1.779(5) Å and [C=C] distances of 1.342(8) and 1.353(8) Å. The [C=C] distance of the double bond linking the two five-membered rings is 1.333(8) Å. Despite the pronounced fold of the TTF unit, the separation between the [C=C] double bond linking the two five-membered rings and the plane of the 1,5-dioxynaphthalene ring system is 3.83 Å, indicative of a weak intramolecular $[\pi\cdots\pi]$ stabilization. The molecules pack to form (Figure 5) offset polar stacks, the 1,5-dioxynaphthalene ring system of one molecule being positioned over the central portion of the TTF unit of the next, with a mean interplanar separation of 3.54 Å, consistent with a significant $[\pi\cdots\pi]$ interaction.

^{1}H NMR Spectroscopy. The pairs of enantiomers *(R/S)-cis*-**4** and *(RR/SS)-trans*-**4** were isolated *(*vide infra*)* by crystallization. Their ^{1}H NMR spectra at ambient temperature in $(CD_3)_2SO$ show three resonances for the 1,5-dioxynaphthalene protons. For *(R/S)-cis*-**4**, these observations imply that the cyclophane is flexible enough[7] to exchange rapidly on the ^{1}H NMR time scale the 1,5-dioxynaphthalene protons in positions 2, 3, and 4 with those in positions 6, 7, and 8, respectively. Three resonances are observed[8] for the bismethylene protons $[SCH^aH^bCH^c_2O]$ of *(R/S)-cis*-**4**, while four signals are associated with the bismethylene protons $[SCH^aH^bCH^cH^dO]$ of *(RR/SS)-trans*-**4**. No significant changes were detected in the ^{1}H NMR spectra upon varying the temperature (300−413 K). These observations mean that the ring inversion (Process I) between the two enantiomers of *(R/S)-cis*-**4**, as well as that (Process I and Process II) between the two enantiomers of *(RR/SS)-*

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(6) For related examples, see: (a) Marcos, C. F.; Rakitin, O. A.; Rees, C. W.; Torroba, T.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 29−30. (b) Konstantinova, L. S.; Rakitin, O. A.; Rees, C. W.; Souvorova, L. I.; Torroba, T.; White. A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 73−74.

(7) In the case of *cis*-**4**, there are only *three* resonances observed for the two sets, namely, (2/3/4) and (6/7/8), of 1,5-dioxynaphthalene protons. This observation can be rationalized by appreciating that the TTF unit can rotate freely over the top of the 1,5-dioxynaphthalene ring system. When the two are orthogonal to each other, a conformation with a C_2 axis is attained wherein the positions (2/3/4) are exchanged by symmetry with the positions (6/7/8) on the 1,5-dioxynaphthalene ring system as a consequence of this “TTF wagging action”.

(8) In principle, four resonances should be observed for the $-SCH_2CH_2O-$ protons of *cis*-**4** as a result of the rapid “TTF wagging action”. In practice, the two OCH_2 proton resonances are accidentally equivalent and only three resonances are actually observed; they persist in the spectrum even up to high temperatures. In the case of *trans*-**4**, all four resonances that are expected for the $-SCH_2CH_2O-$ protons are indeed observed and once again they persist in the spectrum at high temperatures. The conclusion that has to be reached is that neither (*R*)-*cis*-**4**/(*S*)-*cis*-**4** nor (*RR*)-*trans*-**4**/(*SS*)-*trans*-**4** undergo ring inversion on the ^{1}H NMR time scale, i.e., *racemization between the enantiomeric pairs does not occur.*

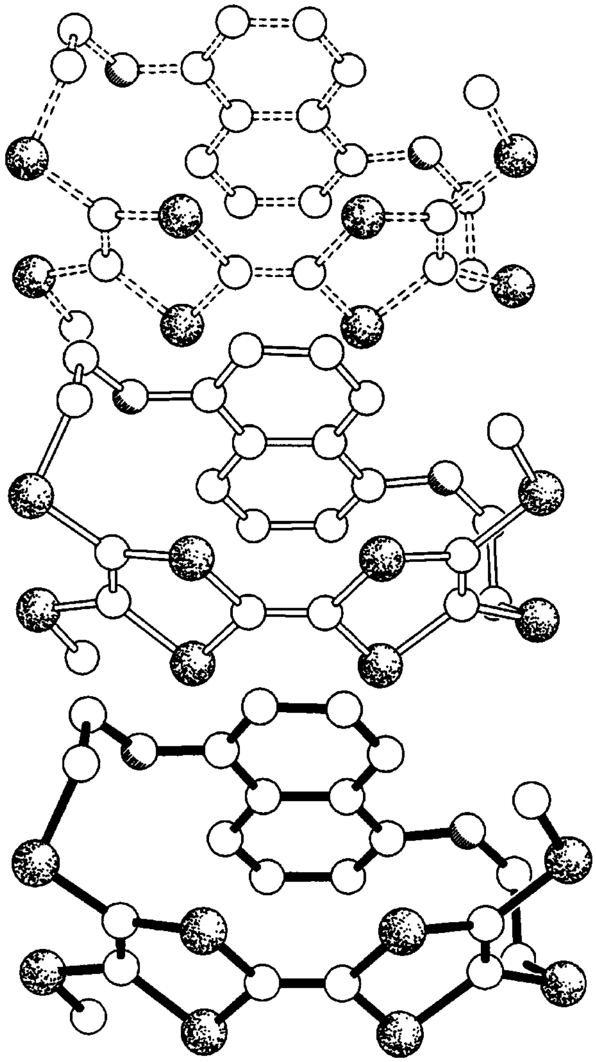

Figure 5. One of the polar stacks formed by *(RR)-trans*-**4** in the solid state.

trans-**4**, *is not occurring on the* ^{1}*H NMR time scale*, otherwise exchange between [SCH^a] and [SCH^b] would be observed. By contrast, the *cis/trans* isomerization of the TTF unit occurs when a $(CD_3)_2SO$ solution of either *(R/S)-cis*-**4** or *(RR/SS)-trans*-**4** is exposed[9] to ambient light, as revealed by the changes in its ^{1}H NMR spectrum. After about 60 h of exposure to ambient light, an equilibrium (photostationary state) between the *cis* and *trans* forms was reached, with a *cis*/*trans* ratio of ca. 1.4. No changes in the isomerization rates were observed when *i*-Pr_2EtN was added to the solution, and no isomerization occurred at all when the solution was maintained in the dark. These observations indicate that the *cis/trans* isomerization is induced by light[4] rather than by traces of acid.[2] It is interesting to note that isomerization of *(R/S)-cis*-**4** can yield *(RR/SS)-trans*-**4**, as well as *(RS/SR)-trans*-**4**, which are nondegenerate *(*vide infra*)*. It is clear from all of the analytical and spectroscopic data that *(RS/SR)-trans*-**4** is not formed as part of the photostationary state established with ambient light.

Molecular Modeling. The diastereoisomers *(R)-cis*, *(RR)-trans*, and *(RS)-trans* were constructed[10] within the build mode of Spartan 4.1, and their geometries were optimized (AM1, Spartan 4.1). The energies of the resulting structures (Figure 6) were determined[11] by single point calculations (HF/3-21G) using Gaussian 94. These calculations revealed that *(R)-cis* is more stable by ca. 3.5 kcal mol^{-1} than *(RR)-trans*, which in turn is more stable than *(RS)-trans* by ca. 1.7 kcal mol^{-1}.

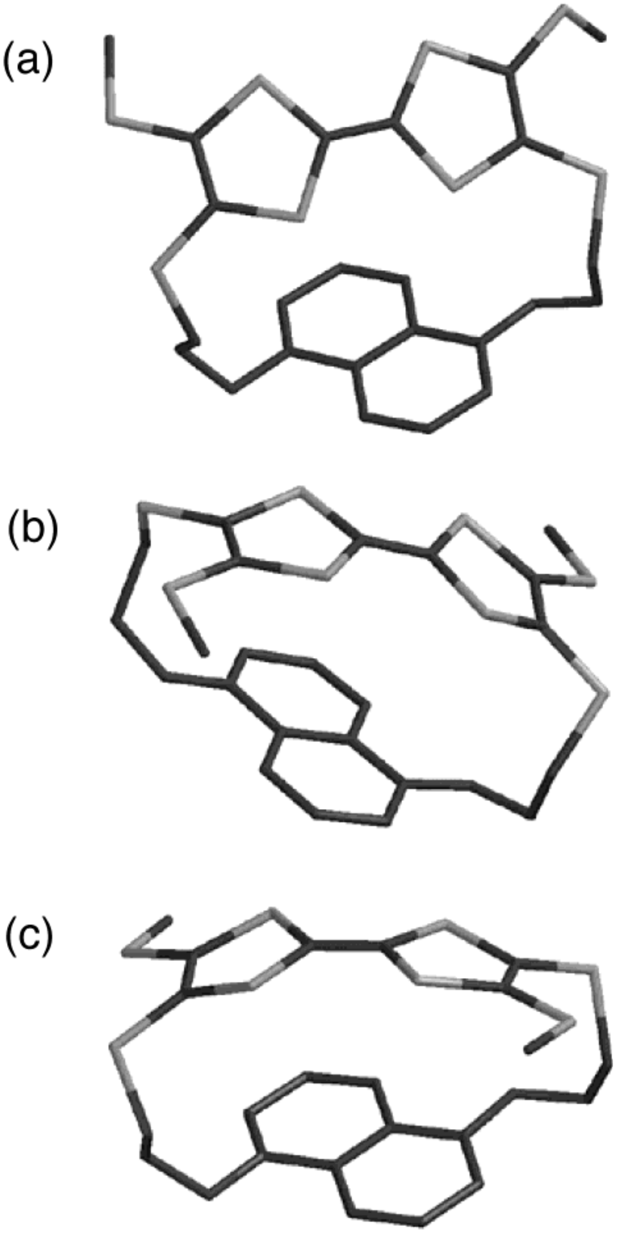

Figure 6. Optimized (AM1) geometries of (a) *(R)-cis*-**4**, (b) *(RR)-trans*-**4**, and (c) *(RS)-trans*-**4**.

Absorption Spectra and Photochemical Behavior. The absorption spectra of *(RR/SS)-trans*-**4** and *(R/S)-cis*-**4** in Me_2SO solution are shown in Figure 7. Comparison with the spectra of 1,5-dimethoxynaphthalene and tetra(methylthio)tetrathiafulvalene, which are model compounds containing the two chromophoric units of **4**, shows that in both isomers (i) the bands at longer wavelength (λ > 340 nm) are associated with the TTF unit, (ii) at shorter wavelength the bands of the 1,5-

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[9] Pyrex glass NMR tubes were used for these experiments.

[10] *Spartan* V 4.1; Wavefunction, Inc.: 18401 Von Karman Ave., #370 Irvine CA 92715, 1995.

[11] *Gaussian 94*, Revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

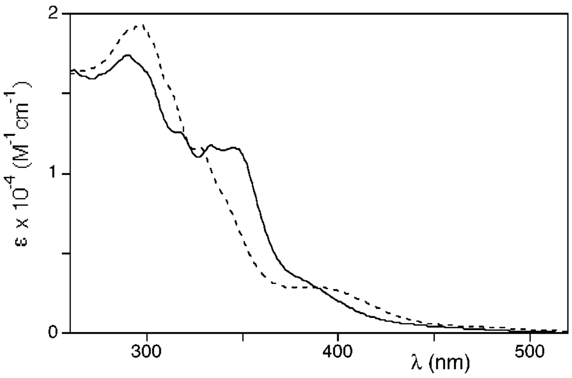

Figure 7. Absorption spectra of *(R/S)-cis*-**4** (dashed line) and *(RR/SS)-trans*-**4** (full line) in Me$_2$SO solution at room temperature.

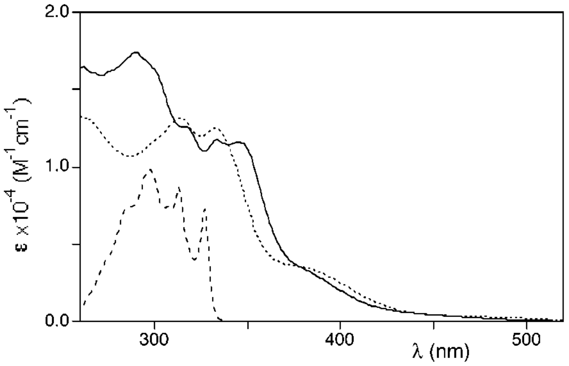

Figure 8. Absorption spectra of *(RR/SS)-trans*-**4** (full line) and of the 1,5-dimethoxynaphthalene (dashed line) and tetra(methylthio)tetrathiafulvalene (dotted line) model compunds of the cyclophane chromophoric units in Me$_2$SO solution at room temperature.

dimethoxynaphthalene and TTF units overlap, and (iii) the two chromophoric units are distorted and/or interact with each other because the spectrum of *(RR/SS)-trans*-**4** (and, not shown, also that of *(R/S)-cis*-**4**) does not match (Figure 8) the sum of the spectra of the two model compounds. We have also found that the well-known fluorescence of the 1,5-dimethoxynaphthalene moiety[12] is not observed in Me$_2$SO solutions of *(RR/SS)-trans*-**4** and *(R/S)-cis*-**4**, regardless of the excitation wavelength. This observation establishes that, in the cyclophanes, the potentially fluorescent excited state of the 1,5-dimethoxynaphthalene unit finds a fast radiationless decay route, presumably because of some kind of interaction with the TTF unit (vide infra).

Although solutions of both isomers were stable when kept in the dark, upon light excitation noticeable spectral changes were observed. Irradiation of a Me$_2$SO solution of *(RR/SS)-trans*-**4** with 406 nm light caused the UV–vis spectral changes shown in Figure 9. Clean isosbestic points, corresponding to those exhibited by the spectra of the pure *(R/S)-cis*-**4** and *(RR/SS)-trans*-**4** forms (Figure 7) were maintained during irradiation. This observation shows that the process taking place is the conversion of the *trans* into the *cis* isomer. The photoreaction quantum yield (Φ, number of isomerized molecules/number of photons absorbed), measured from the changes in absorbance, was found to be 0.20. Irradiation of *(RR/SS)-trans*-**4** with light of 313 nm again caused the *trans* → *cis* photoisomerization reaction, but with a smaller quantum yield ($\Phi = 0.11$). The decrease in the photoreaction quantum yield, on passing from 406 to 313 nm excitation, shows that the fraction of light absorbed by the 1,5-dimethoxynaphthalene chromophoric unit upon 313 nm excitation (Figure 8) is not useful for the isomerization of the TTF-type unit. Since the fluorescence of 1,5-dimethoxynaphthalene was not observed, we conclude that the 1,5-dimethoxynaphthalene excited state of *(RR/SS)-trans*-**4** undergoes a radiationless decay that, however, does not involve energy transfer to the TTF unit.

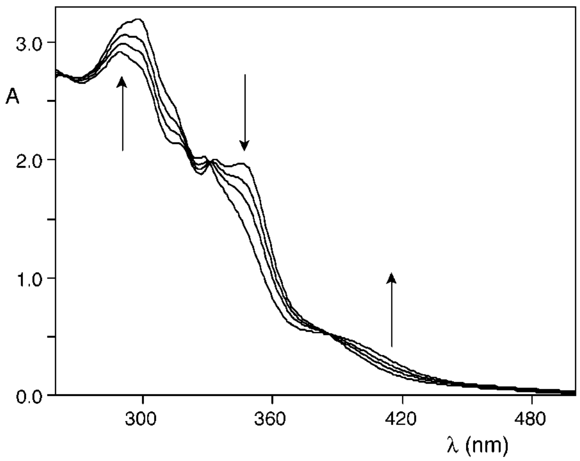

Figure 9. Spectral changes observed upon irradiation of a 1.5×10^{-4} M Me$_2$SO solution of *(RR/SS)-trans*-**4** with 406 nm light at room temperature.

Irradiation of *(R/S)-cis*-**4** with 406 nm light in Me$_2$SO solution caused spectral changes with the same isosbestic points as those shown in Figures 7 and 9, indicating the occurrence of the *cis* → *trans* photoisomerization. The quantum yield of this reaction ($\Phi = 0.030$ at 406 nm) is much smaller than that of the *trans* → *cis* process (*vide supra*). The quantum yield for the *cis* → *trans* photoisomerization reaction is constant in going from the visible to the UV spectral region ($\Phi = 0.030$ at 313 nm), despite the competition for the exciting light between the TTF and 1,5-dimethoxynaphthalene chromophoric units when excitation is performed at 313 nm (see Figures 7 and 8). This result indicates that, in the case of *(R/S)-cis*-**4**, an efficient energy-transfer process takes place from the 1,5-dimethoxynaphthalene to the TTF unit. The reason for the different kind of interaction between the two chromophoric units in the *cis* and *trans* isomers is not clear, but it has to be related to the different structures of the two isomers (Figures 2 and 4).

Since both *(RR/SS)-trans*-**4** and *(R/S)-cis*-**4** absorb light and both undergo photoisomerization, the above-reported quantum yields have been obtained by extrapolation to zero time of the (uncorrected) quantum yield values obtained at different irradiation times. On prolonged irradiation, a photostationary state is reached in all cases (for example, see Figure 10). Since the absorption spectra of the *(RR/SS)-trans*-**4** and *(R/S)-cis*-**4** isomers are different from one another (Figure 7) and the quantum yields of the *trans* → *cis* photoisomerization reaction is wavelength dependent, the mole fractions of the two isomers present at a photostationary state depend on the wavelength of the incident light. In the

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[12] Ballardini, R.; Balzani, V.; Gandolfi, M. T.; Gillard, R. E.; Stoddart. J. F.; Tabellini, E. *Chem. Eur. J.* **1998**, *4*, 449–459.

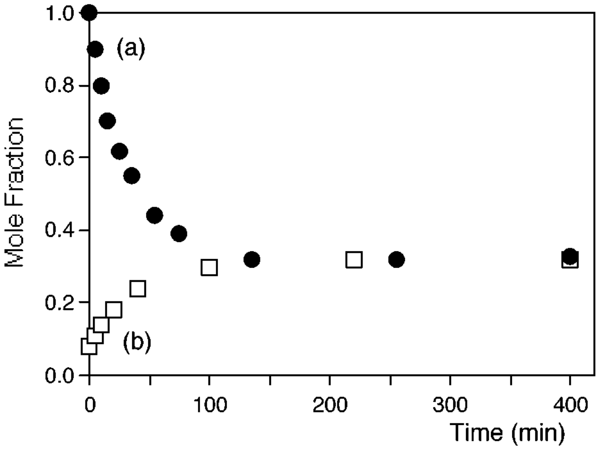

Figure 10. Plot of the mole fraction of *(RR/SS)-trans*-**4** against irradiation time (406 nm light, Me_2SO solution, room temperature): (a) starting from a solution containing pure *(RR/SS)-trans*-**4** and (b) starting from a solution containing 92% *(R/S)-cis*-**4** and 8% *(RR/SS)-trans*-**4**. Both of the initial solutions are completely stable in the dark, as is the solution obtained after prolonged irradiation.

case of excitation with 406 nm light (Figure 10), the mole fraction of the *trans* isomer at the photostationary state is 32%.

Electrochemical Data. No difference in redox potentials were observed between *(R/S)-cis*-**4** and *(RR/SS)-trans*-**4**. For both cyclophanes in CH_2Cl_2 cyclic voltammetry afforded the values $E_{1/2}{}^1 = 0.50$ V, $E_{1/2}{}^2 = 0.94$ V (vs Ag/AgCl, supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate). The first potential is significantly diminished relative to that of tetra(methylthio)tetrathiafulvalene ($E_{1/2}{}^1 = 0.56$ V, $E_{1/2}{}^2 = 0.91$ V, in CH_2Cl_2), which is in accordance with a stabilizing influence exerted by the dioxynaphthalene donor on the generated radical cation.

Conclusions

A chiral cyclophane,[13] incorporating one TTF unit and one 1,5-dioxynaphthalene ring system, has been synthesized. As a result of the *cis/trans* isomerization of the TTF unit and of the elements of planar chirality imposed by the *trans*-TTF unit and by the 1,5-dioxynaphthalene ring system, three pairs of enantiomers are possible for this cyclophane. Two of these three pairs were isolated by crystallization, and their structures were analyzed by single-crystal X-ray analyses. No isomerization occurs when Me_2SO solutions of *(RR/SS)-trans*-**4** and *(R/S)-cis*-**4** are maintained in the dark. Upon light excitation, both the *trans* and the *cis* isomers undergo photoisomerization, leading to a photostationary state. The photoisomerization quantum yield is much higher for the *trans* → *cis* than for the *cis* → *trans* process. Only in the case of the *(R/S)-cis*-**4** isomer is excitation (313 nm) of the 1,5-dioxynaphthalene unit followed by energy transfer to the TTF unit.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry Ar. MeOH was distilled from Mg and I_2, and DMF was allowed to stand over molecular sieves (4 Å) for at least 3 d before use. Me_2CO was dried using Drierite. 2,3,6,7-Tetrakis(2′-cyanoethyl-thio)tetrathiafulvalene (**3**) was synthesized according to a literature procedure.[14] HPLC separations were carried out using a gradient elution of mixtures of hexane/$MeCO_2Et$ (from 100:0 to 50:50 over 25 min) on a 10 μm Si-prep 250 mm × 4.6 mm column with a flow rate of 1 mL/min. The sample was injected from a CH_2Cl_2 solution. Peak absorptions ($\lambda > 250$ nm) are reported relative to the peak with highest absorbance. Absorption spectra were recorded in Me_2SO solution. The photochemical experiments were carried out in a cell (capacity, 3 mL; optical path, 1 cm) filled with an air-equilibrated ca. 1.0×10^{-4} M solution. Light excitation at 406 and 313 nm was performed with a medium-pressure mercury lamp, using interference filters. The incident light intensity (of the order of 1×10^{-7} N$h\nu$/min) was measured by the microversion of the ferric oxalate actinometer.[15] The concentration of the *cis* and *trans* isomers after selected irradiation times was obtained from the measured absorbance values at two different wavelengths. Since both isomers absorb light and undergo photoisomerization, the quantum yield of each photoreaction was obtained by extrapolating to zero time the experimental values obtained after different irradiation periods. The experimental error on the values of the corrected quantum yields is estimated to be ±15%. NMR spectra were obtained using a 400 MHz spectrometer with the solvents being employed as internal standards. Cyclic voltammetry was performed using n-Bu_4NPF_6 as the supporting electrolyte. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl.

1,5-Bis(2-bromoethoxy)naphthalene (2). A mixture of 1,5-dihydroxynaphthalene (**1**) (2.53 g, 15.8 mmol), K_2CO_3 (3.00 g, 21.7 mmol), and 1,2-dibromoethane (20 mL) in dry Me_2CO (150 mL) was heated under reflux for 12 h. After additional portions of K_2CO_3 (3.00 g, 21.7 mmol) and 1,2-dibromoethane (20 mL) had been added, the solution was heated under reflux for a further 12 h. After cooling to ambient temperature, the mixture was filtered, and the solvent was distilled off under reduced pressure. The residue was washed with CH_2Cl_2, and the organic phase was extracted with H_2O and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2, CH_2Cl_2) to yield the dibromide **2** (875 mg, 15%) as a white solid: mp 157.5−158.5 °C; FABMS m/z 372 $[M]^+$; ^1H NMR ($CDCl_3$) δ 3.78 (t, $J = 6$ Hz, 4H), 4.47 (t, $J = 6$ Hz, 4H), 6.85 (d, $J = 8$ Hz, 2H), 7.38 (t, $J = 8$ Hz, 2H), 7.92 (d, $J = 8$ Hz, 2H). Anal. ($C_{14}H_{14}Br_2O_2$): calcd C 44.95, H 3.77; found C 44.60, H 3.62.

2,7(6)-Bis(methylthio)-3,6(7)-[naphthalene-1,5-diyldioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene (4). A solution of $CsOH{\cdot}H_2O$ (296 mg, 1.76 mmol) in MeOH (10 mL) was added to a solution of **3** (374 mg, 0.80 mmol) in DMF (50 mL) over 10 min. The resulting solution was stirred for 30 min at ambient temperature. This solution and a solution of the dibromide **2** (300 mg, 0.80 mmol) in DMF (60 mL) were added simultaneously, using a two-syringe perfusor pump, to DMF (100 mL) during 12 h. The resulting solution was stirred for 2 h at ambient temperature, and then the solvent was distilled off under reduced pressure. The solid residue was dissolved in CH_2Cl_2, washed with H_2O, and dried ($MgSO_4$). The solvent was distilled off under reduced pressure and the residue was purified by column chromatography (SiO_2/CH_2Cl_2) to afford the

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cyclophane **4** (309 mg, 67%) as an orange solid. **4**: HRMS (FAB) *m*/*z* calcd for $[M]^+$ 571.9229, found 571.9230. Anal. ($C_{22}H_{20}O_2S_8$): calcd C 46.13, H 3.52; found C 45.87, H, 3.42. *(R/S)-cis*-**4**: ^{1}H NMR [$(CD_3)_2SO$] δ 2.54 (s, 6H), 3.02 (dt, J = 15 and 4 Hz, 2H), 3.29 (dt, J = 15 and 7 Hz, 2H), 4.56 (dd, J = 7 and 4 Hz, 4H), 7.01 (d, J = 8 Hz, 2H), 7.39 (t, J = 8 Hz, 2H), 7.63 (d, J = 8 Hz, 2H); HPLC t_R 14.7 min [UV ($\lambda > 250$ nm, nm = 293 (100%), 326 (57%), 392 (13%). Crystallization from CH_2Cl_2/hexane afforded an amorphous solid together with needles of *(R/S)-cis*-**4** that were suitable for X-ray crystal structure analysis. X-ray data: $C_{22}H_{20}O_2S_8{\cdot}{}^1/_8CH_2Cl_2{\cdot}{}^1/_3C_6H_{14}$, M = 612.2, rhombohedral, $R\bar{3}$ (no. 148); $a = b = 37.753(3)$, $c = 10.088(1)$ Å, $V = 12452(2)$ Å^3, $Z = 18$, $D_c = 1.470$ g cm^{-3}, μ(Cu Kα) = 63.8 cm^{-1}, $F(000) = 5723$, $T = 173$ K; orange hexagonal needles, 0.63 mm × 0.06 mm × 0.06 mm, Siemens P4/RA diffractometer, ω-scans, 3980 independent reflections, semiempirical absorption correction, max. and min. transmission factors 0.90 and 0.73, respectively. The structure was solved by direct methods, and the major occupancy non-hydrogen atoms of the cyclophane were refined anisotropically; only the chlorine atom of the disordered solvent molecules was refined anisotropically, the other non-hydrogen atoms being refined isotropically. The hydrogen atoms of the cyclophane were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, $[U(H) = 1.5U_{eq}(C{-}Me)]$, and allowed to ride on their parent atoms. The hydrogen atoms of the included solvent molecules were not located. Refinements were by full matrix least-squares based on F^2 to give $R_1 = 0.054$, $wR_2 = 0.122$ for 2948 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$] and 341 parameters. CCDC-137705. *trans*-**4**-*(RR/SS)*: ^{1}H NMR [$(CD_3)_2SO$] δ 2.57 (s, 6H), 3.08 (dd, J = 15 and 2 Hz, 2H), 3.67 (ddd, J = 15,11 and 2 Hz, 2H), 4.42 (ddd, J = 11, 11 and 2 Hz, 2H), 4.87 (dd, J = 11 and 2 Hz, 2H), 6.94 (d, J = 8 Hz, 2H), 7.26 (t, J = 8 Hz, 2 H), 7.55 (d, J = 8 Hz, 2H); HPLC t_R 15.5 min [UV ($\lambda > 250$ nm, nm = 285 (100%), 315 (66%), 332 (67%), 385 (15%) nm. Blocky rhomb-like crystals of *(RR/SS)-trans*-**4** were obtained using the same solvent mixture. These crystals were dissolved in CH_2Cl_2, and after the liquid/liquid diffusion of hexane, single crystals suitable for X-ray analysis were obtained. X-ray data: $C_{22}H_{20}O_2S_8$, M = 572.9, triclinic, $P\bar{1}$ (no. 2); $a = 7.409(1)$, $b = 10.443(1)$, $c = 16.701(1)$ Å, $\alpha = 85.01(1)$, $\beta = 85.22(1)$, $\gamma = 69.27(1)°$, $V = 1202.0(1)$ Å^3, $Z = 2$, $D_c = 1.583$ g cm^{-3}, μ(Cu Kα) = 70.5 cm^{-1}, $F(000) = 592$, $T = 183$ K; yellow rhombs, 0.23 mm × 0.20 mm × 0.20 mm, Siemens P4/RA diffractometer, ω-scans, 3772 independent reflections, semiempirical absorption correction, max. and min. transmission factors 0.31 and 0.19, respectively. The structure was solved by direct methods, and the non-hydrogen atoms refined anisotropically. The hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, $[U(H) = 1.5U_{eq}(C{-}Me)]$, and allowed to ride on their parent atoms. Refinements were by full matrix least-squares based on F^2 to give $R_1 = 0.059$, $wR_2 = 0.152$ for 3236 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 124°$] and 290 parameters. CCDC-137706.

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Supporting Information Available: Tables of X-ray structural data for compounds (*R*/*S*)-*cis*-**4** and (*RR*/*SS*)-*trans*-**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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