Syntheses and Structural Analysis of 10-Monoxy- and -Dioxy-5-*N*-Substituted Iminothianthrene Derivatives and the Stereochemical Change on their Sulfur Atom under Acidic and Thermal Conditions

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Dedicated to Professor Shigeru Oae on the occasion of his 80th birthday

Abstract: 5-(*N*-*p*-Toluenesulfonyl)iminothianthrenes, whose sulfur atoms are oxidized to a sulfoxide or sulfone at the 10-position, were hydrolysed readily in high yield to *N*-unsubstituted-sulfilimines by using concentrated H_2SO_4. During hydrolysis, 10-monoxy-5-*N*-unsubstituted-sulfilimines were obtained as a separable mixture of the *cis* and *trans* isomers. The stereochemical interconversion of these compounds was studied under both hydrolytic and thermal conditions and their structures were elucidated by using X-ray crystallography.

Keywords: steric hindrance · structure–activity relationships · substituent effects · sulfilimines · sulfur · thianthrene derivatives

Introduction

To date only a limited number of reports on the sulfur chemistry of thianthrene, such as its oxidation to sulfoxides and sulfones, and its imination to sulfilimine derivatives,[1] have appeared in the literature. Recently, Bonchio et al.,[2] and Adam et al.[3] noted the importance of steric and electronic effects on both the rate and the site of further oxidation of thianthrene or the 5-oxide to their oxides under several oxidation conditions. *N*-Unsubstituted-sulfilimines are readily obtained by hydrolysis of their *N*-*p*-toluenesulfonyl precursors with concentrated H_2SO_4.[4] However, this method is not applicable to thianthrene sulfilimine precursors because of their instability in concentrated H_2SO_4 and the subsequent formation of a radical cation intermediate. We have found that 5-(*N*-*p*-toluenesulfonyl)iminothianthrenes, with an oxidized sulfur atom in the form of sulfoxide or sulfone at the 10-position, were converted to *N*-unsubstituted-sulfilimines in good yields by the same procedure. Thus, we have been able to prepare several 10-monoxy- and -dioxy-5-*N*-unsubstituted iminothianthrenes. The *cis* and *trans* isomers of 10-monoxy-5-*N*-unsubstituted- and -5-*N*-substituted iminothianthrenes were separated and their interconversion studied under both hydrolytic conditions in acidic media and thermal conditions. X-ray crystallographic analyses for both thianthrene itself and several oxidized thianthrenes reported by Lynthon and Cox,[5] Row and Post,[6] and Hosoya,[7] show that thianthrene derivatives are folded along the S–S axis, and consequently exist as "butterfly structures", which contain a boat-form similar to a 1,4-dithiin structure for the center 6-membered ring of thianthrene as reported by Lipscomb et al.[8] From these structures it is evident that a direct interaction between the substituents on the two sulfur atoms can occur; this could well be the cause for the difference in reactivities on the sulfur atoms between *cis* and *trans* isomers. The results of X-ray crystallographic analyses of these sulfilimine derivatives are also described here.

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Results and Discussion

5-(*N*-*p*-Toluenesulfonyl)iminothianthrene **1** was readily obtained by the reaction of the sodium salt of *N*-chloro-*p*-toluenesulfonamide (chloramine T) in CH_3CN. The iminothianthrene derivative **1** was oxidized with 3-chloroperoxy-

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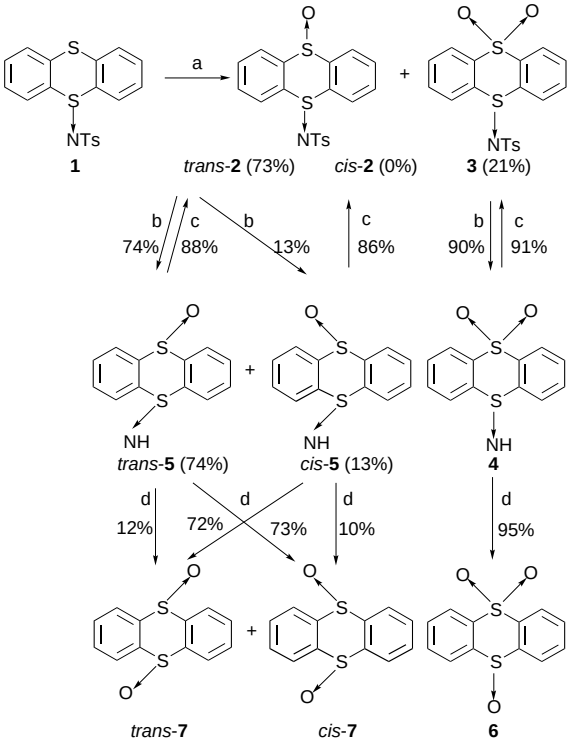
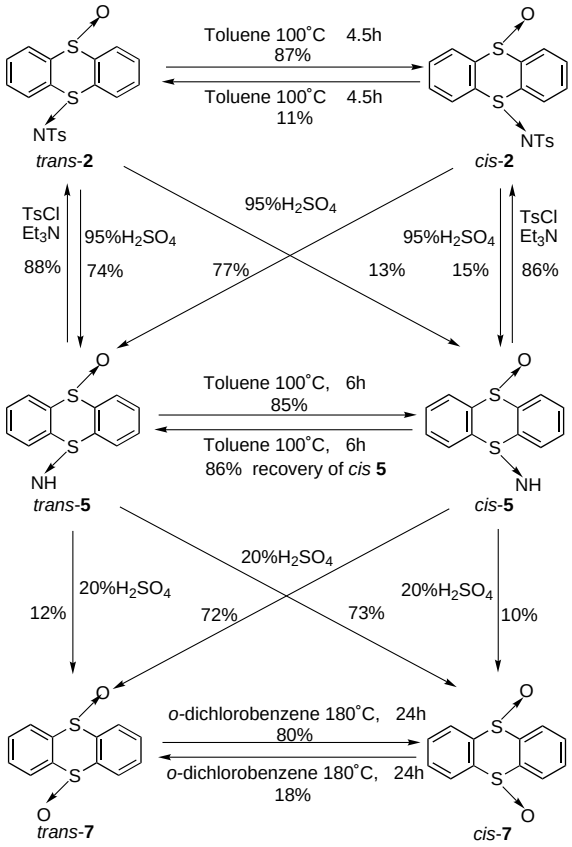
benzoic acid (*m*-CPBA) in CH_2Cl_2 at room temperature to afford the corresponding 10-*S*-monoxy- (*trans*-**2**) and 10-dioxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (**3**) in 73 and 21% yield, respectively (Scheme 1). During the oxidation reaction of **1**, the formation of *cis*-10-monoxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (*cis*-**2**) was not observed, even by ^{1}H NMR analysis, this is probably due to rapid oxidation to the corresponding dioxy derivative **3**. This explanation is supported by a recent report which shows that the oxidation of *cis*-thianthrene-5,10-dioxide with MoO_5 was 5.6 times faster than that of *trans*-thianthrene-5,10-dioxide.[2]



Scheme 1. a) m-CPBA, CH_2Cl_2, RT. b) 95% H_2SO_4, RT, then aq. KOH. c) TsCl/Et_3N, CH_2Cl_2; RT, d) 20% H_2SO_4, 65 °C, 3 h.

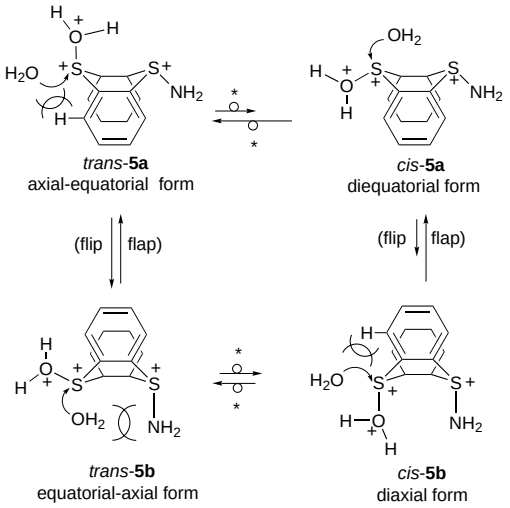
Acidic hydrolysis of N–Ts to N–H in concentrated H_2SO_4: 10-Dioxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (**3**) was treated with concentrated H_2SO_4 at room temperature to afford *N*-unsubstituted-sulfilimine **4** in high yield. Similarly, *trans*-10-monoxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (*trans*-**2**) was hydrolyzed with concentrated H_2SO_4 to give a mixture of the corresponding *trans*- and *cis*-*N*-unsubstituted-sulfilimines (*trans*- and *cis*-**5**), in the respective ratio 74:13 as determined by ^{1}H NMR analysis. This mixture was further separated and purified by repeated recrystallization. The structures of *trans*- and *cis*-**5** were confirmed by tosylating them, to give the starting products *trans*- and *cis*-**2**, respectively (Scheme 1). Compound *cis*-**2** thus obtained, or isomerized thermally from *trans*-**2** (in toluene, 100 °C, as described later), was also hydrolyzed under the same conditions as in the case of *trans*-**2** described earlier (95% H_2SO_4), to result in almost the same respective mixture ratio (77:15) of *trans*- and *cis*-**5** (see Scheme 2).



Scheme 2.

It has been reported that optically active sulfoxides in H_2SO_4 undergo oxygen exchange reactions concurrently with racemization reactions, changing the mechanism from A1 to A2 type depending on the concentration of the acid.[9] Therefore, the results shown in Scheme 2 are simply accounted for by the inversion of the sulfinyl group by substitution of H_2O on the hydroxysulfonium sulfur atom at the 10-position formed by protonation in the course of hydrolysis in concentrated H_2SO_4, because the cleavage of the N–Ts bond evidently does not involve the inversion process.[10] In a control experiment, the ratio of *trans*-**5** and *cis*-**5** in concentrated H_2SO_4 (commercial; 95%) was observed as 6:1 by ^{1}H NMR analysis after 10 min of equilibration and workup. This ratio is almost the same as that observed for the hydrolysis of the N–Ts bond of *trans*-**2** and *cis*-**2** to the corresponding *N*-unsubstituted-sulfilimines under the same acidic conditions. Thianthrene derivatives are known to be in an equilibrium state, consisting of a mixture of the so-called "flip-flap" isomers, which are interconvertible around the S–S axis of the dithiin framework.[11]

In Scheme 3 two possibilities of such "flip-flap" conformers for both the protonated *trans*-**5** and *cis*-**5** are illustrated schematically. They consist of two *trans* forms that are almost energetically the same, the axial (S–O)/equatorial (S–NH) form (*trans*-**5a**) and the equatorial (S–O)/axial (S–NH) form (*trans*-**5b**), and the apparently energetically different *cis* forms, the diequatorial (S–O, S–NH) form (*cis*-**5a**) and the diaxial (S–O, S–NH) form (*cis*-**5b**). Compound *cis*-**5a** is more stable than *cis*-**5b** due to the diaxial repulsion between the



Scheme 3.

S–O and S–NH groups. From a comparison of the four forms in Scheme 3, it is evident that the *trans* form (*trans*-**5b** or *trans*-**5b**) seems to be less easily attacked by H_2O than the *cis* form (*cis*-**5a**) because of unfavorable steric hindrance by the peri hydrogens on the two benzene rings (*trans*-**5a** case) or the axial S–NH group (*trans*-**5b** case), although Scheme 3 depicts the A2 mechanism. However, the steric situation with regard to the attacking site for H_2O is predicted to be almost the same even in the A1 case. Therefore, in concentrated H_2SO_4 the differences in the steric environment of the four conformers suggest that the *trans* isomer is thermodynamically more stable than the *cis* isomer, and that the *cis* isomer is more easily attacked by H_2O than the *trans* isomer. Hence, in the hydrolytic conversion of both *trans*-**2** and *cis*-**2** to the *N*-unsubstituted-sulfilimines, the more stable *trans*-**5** is more favorably formed than *cis*-**5**. Interestingly, this is in contrast to the greater thermodynamic stability of *cis*-**2**, as mentioned later (see also Scheme 2), and is the first example of a direct comparison of the replacement ability by H_2O in H_2SO_4 between the NH group (*N*-unsubstituted-sulfilimine) and oxygen (sulfoxide) on the sulfur atom in the same molecule. The oxygen exchange proceeds preferentially over de-imination. Nevertheless, the leaving ability of the amino group is expected to be larger than that of the hydroxy group on a sulfonium sulfur atom in compound **5**, as depicted in Scheme 3. Actually, *N*-unsubstituted-sulfilimines (pK_a value of the conjugate acid for diphenyl unsubstituted-sulfilimine: 8.56[12]) are more basic than sulfoxides (pK_a value of the conjugate acid for diphenyl sulfoxide: -4.97[13]). Therefore, the former can be a good leaving group after double protonation in concentrated H_2SO_4.

All the structural data for *trans*-**2**, *cis*-**2**, **3**, **4**, *trans*-**5**, and *cis*-**5**, such as ^1H NMR, ^{13}C NMR, and IR spectroscopy, mass spectrometry, and elemental analyses, are consistent with the expected structures. The final structure confirmations for *trans*-**2**, *cis*-**2**, **3**, and *trans*-**5** were performed by single crystal X-ray crystallographic analyses as shown by the ORTEP drawings in Figure 1–4, respectively. The structure for *cis*-**5b** is unavailable because of the difficulty of obtaining suitable single crystals. The crystal structure of the *N*-unsubstituted-sulfilimine of *trans*-**5** is the first reported example by X-ray crystallography for these compounds, as single crystals are usually unstable under X-ray irradiation. The stereochemistry of the crystal structures, *trans*-**2**, *cis*-**2**, **3**, and *trans*-**5**, is consistent with that proposed in this paper.

All the sulfilimines, *trans*-**2**, *cis*-**2**, **3**, **4**, *trans*-**5**, and *cis*-**5** have strong IR bands around 900–1000 cm^{-1}, which were assigned to the ν (S–N) stretching vibrations. Other strong absorption bands for *trans*-**2**, *cis*-**2**, *trans*-**5**, and *cis*-**5** appear in the region 1010–1080 cm^{-1} due to ν (S–O) stretches; this

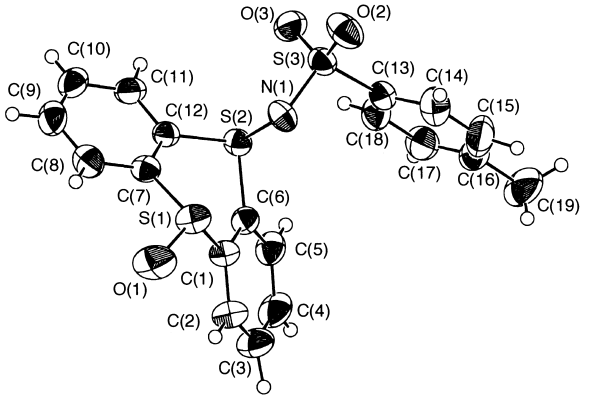


Figure 1. An ORTEP drawing of *trans*-**2** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: S(1)–O(1), 1.481(1); S(1)–C(1),1.790(1); S(1)–C(7), 1.798(1); S(2)–N(1), 1.634(1); S(2)–C(12), 1.775(1); S(2)–C(6), 1.771(1); S(3)–O(2), 1.436(1); S(3)–O(3), 1.436(1); S(3)–N(1), 1.626(1); S(3)–C(13), 1.772(1); O(1)–S(1)–C(1), 107.8(1); C(7)–S(1)–O(1), 106.5(1); C(7)–S(1)–C(1), 96.3(1); N(1)–S(2)–C(12), 105.7(1); N(1)–S(2)–C(6), 105.3(1); C(12)–S(2)–C(6), 99.7(1); O(2)–S(3)–O(3), 117.0(1); O(2)–S(3)–N(1), 105.5(1); O(2)–S(3)–C(13), 108.2(1); O(3)–S(3)–N(1), 111.9(1); O(3)–S(3)–C(13), 107.6(1); N(1)–S(3)–C(13), 106.1(1); S(2)–N(1)–S(3), 111.5(1).

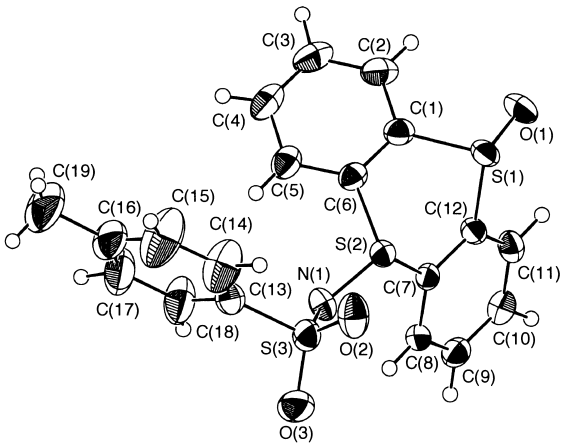


Figure 2. An ORTEP drawing of *cis*-**2** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: S(1)–O(1), 1.491(1); S(1)–C(1), 1.817(1); S(1)–C(12), 1.825(1); S(2)–N(1), 1.620(1); S(2)–C(6), 1.811(1); S(2)–C(7), 1.811(1); S(3)–O(2), 1.459(1); S(3)–O(3), 1.460(1); S(3)–N(1), 1.638(1); S(3)–C(13), 1.792(1); O(1)–S(1)–C(1), 108.4(1); O(1)–S(1)–C(12), 107.4(1); C(1)–S(1)–C(12), 93.5(1); N(1)–S(2)–C(6), 107.4(1); N(1)–S(2)–C(7), 104.0(1); C(6)–S(2)–C(7), 95.6(1); O(2)–S(3)–O(3), 117.8(1); O(2)–S(3)–N(1), 113.3(1); O(2)–S(3)–C(13), 107.3(1); O(3)–S(3)–N(1), 106.4(1); O(3)–S(3)–C(13), 107.8(1); N(1)–S(3)–C(13), 103.2(1); S(2)–N(1)–S(3), 114.3(1).

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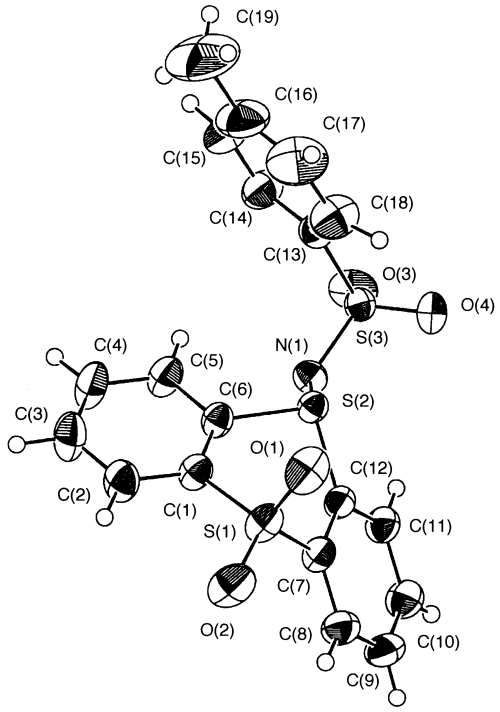

Figure 3. An ORTEP drawing of **3** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: S(1)–O(1), 1.437(1); S(1)–O(2), 1.430(1); S(1)–C(1), 1.765(1); S(1)–C(7), 1.767(1); S(2)–N(1), 1.618(1); S(2)–C(6), 1.795(1); S(2)–C(12), 1.794(1); S(3)–O(3), 1.435(1); S(3)–O(4), 1.436(1); S(3)–N(1), 1.622(1); S(3)–C(13), 1.771(1); O(1)–S(1)–O(2), 119.8(1); O(1)–S(1)–C(1), 107.4(1); O(1)–S(1)–C(7), 107.4(1); O(2)–S(1)–C(7), 100.9(1), N(1)–S(2)–C(6), 102.6(1); N(1)–S(2)–C(12), 105.0(1); C(6)–S(2)–C(12), 98.8(1); O(3)–S(3)–O(4), 118.4(1); O(3)–S(3)–N(1), 104.4(1); O(3)–S(3)–C(13), 107.8(1); O(4)–S(3)–N(1), 112.0(1); O(4)–S(3)–C(13), 107.0(1); N(1)–S(3)–C(13), 106.7(1); S(2)–N(1)–S(3), 113.3(1).

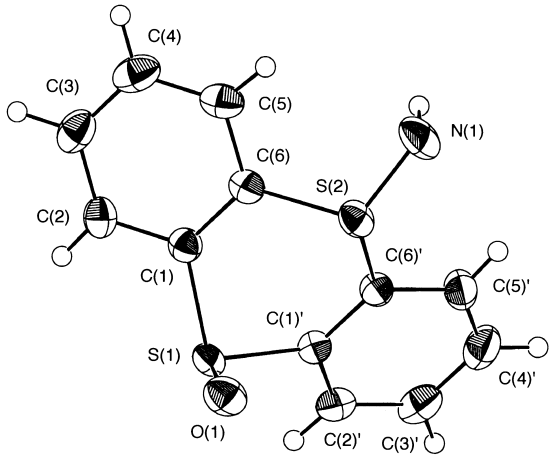

Figure 4. An ORTEP drawing of *trans*-**5** (50% probability ellipsoids). The primed atoms are related to the normal labels by a crystallographic mirror plane at $y = 0.25$. Selected bond lengths [Å] and angles [°]: S(1)–O(1), 1.512(1); S(1)–C(1), 1.794(1); S(2)–N(1), 1.580(1); S(2)–C(6), 1.812(1); N(1)–H(1), 0.941(10); O(1)–S(1)–C(1), 105.9(1); O(1)–S(1)–C(1), 97.4(1); N(1)–S(2)–C(6), 111.0(1), C(6)–S(2)–C(6), 97.4(1).

suggests that the absorption band of the axial conformation is considerably lower than that of the equatorial one, by between 60–80 cm^{-1}. This means that the NTs group of *trans*-**2** and the oxygen atom of *trans*-**5** are evidently in the axial position as seen in the X-ray structure, although this conformation may only exist in the solid state. In *trans*-**2**, the axial S–N bond absorption appears at 920 cm^{-1}, lower than the equatorial S–N bond absorption (1000 cm^{-1}) of the *cis*-**2**. Furthermore, in *trans*-**5** the axial S–O bond absorption appears at 1010 cm^{-1}, which is lower than the equatorial S–O bond absorption (1070 cm^{-1}) of *cis*-**5**, while the other absorption bands at the same equatorial conformation appear at the same or almost the same wave number; namely, 1080 cm^{-1} for ν(S–O) of *trans*-**2** and *cis*-**2**, and 930 and 935 cm^{-1} for ν(S–N) of *trans*-**5** and *cis*-**5**, respectively, as shown in Table 1.

The S–N and S–O bond lengths appear to be affected by both a conformational factor and a substituent effect. Examination of the S–N bond lengths and IR stretching band for S–NH and for S–NTs at the same equatorial position reveals that while the S–N bond length is shorter in *trans*-**5** (1.580(1) Å) than in *cis*-**2** (1.620(1) Å) or **3** (1.618(1) Å), the ν (S–N) stretching band of *trans*-**5** (930 cm^{-1}) is lower than those of *cis*-**2** (1000 cm^{-1}) and **3** (950 cm^{-1}); this is contrary to what was expected. The higher stretching frequency of *N*-tosylsulfilimine relative to the *N*-unsubstituted sulfilimine may be attributed to the coupling of the two S–N stretching bands of both the sulfinyl and sulfonyl S–N bonds. The S–N and S–O bond lengths at the axial position are a little longer than those at the equatorial position; the axial S–NTs bond of *trans*-**2** is 0.014 Å longer than that of *cis*-**2** (equatorial), and the S–O bond of *trans*-**5** (axial) is longer than those of *trans*-**2** and *cis*-**2** by 0.031 Å and 0.021 Å, respectively. A similar result is observed for the IR ν (S–O) stretching bands for *trans*- and *cis*-thianthrene-5,10-dioxide (*trans*-**7** and *cis*-**7**). Compound *cis*-**7** shows only one absorption band, ν (S–O) 1090 cm^{-1}, while *trans*-**7** has two absorption bands, ν (S–O) 1025 and 1070 cm^{-1}; this suggests that the 45 cm^{-1} lower absorption band is due to the axial configuration on the thianthrene sulfur atom. Similar findings have also been reported in the literature.[14]

Acidic hydrolysis of S–NH to S–O of *trans*- and *cis*-5 in 20% aqueous H_2SO_4: The hydrolysis of alkyl aryl sulfilimines is

Table 1. Bond lengths [Å] and their IR stretching frequencies [cm^{-1}] of *trans*-**2**, *cis*-**2**, **3**, *trans*-**5**, and *cis*-**5**.

	trans-**2**		*cis*-**2**		**3**		*trans*-**5**		*cis*-**5**	
bond	S-N	S-O	S-N	S-O	S-N	SO_2	S-N	S-O	S-N	S-O
position[a]	ax	eq	eq	eq	eq		eq	ax	(eq)[b]	(eq)[b]
bond length [Å][c]	1.634	1.481	1.620	1.491	1.618	1.437[d] 1.430[e]	1.580	1.512		
$\tilde{\nu}$ [cm^{-1}][f]	920	1080	1000	1080	950	1160 1320[g]	930	1010	935	1070

[a] Configurational position from X-ray analysis. ax = axial, eq = equatorial. [b] Configurational position estimated. [c] Bond length from X-ray crystallography for S–N or S–O bond. [d] Axial position from X-ray analysis. [e] Equatorial position from X-ray analysis. [f] IR stretching vibration frequency for S–N or S–O bond. [g] ν SO_2.

known to give the corresponding sulfoxide under both acidic and basic conditions. Stereochemical studies indicate that hydrolysis under alkaline conditions proceeds through an inversion mechanism on the sulfur atom, while under acidic conditions the reactions are not stereospecific and yield the completely racemized sulfoxides.[4, 15] In order to study the stereochemistry of the iminothianthrene derivatives under similar acidic conditions, we carried out the hydrolysis reaction of the S–NH bond of **4**, *trans*-**5**, and *cis*-**5** with aqueous 20% H_2SO_4 at 65 °C for three hours. The results are illustrated in Scheme 1. The hydrolysis of **4** gave thianthrene trioxide **6** in high yield. The hydrolysis of *trans*-**5** under the same conditions gave *cis*-**7** in 73% yield together with *trans*-**7** in 12% yield as a minor product. The same hydrolysis of the *cis*-**5** gave *cis*-**7** in 10% yield and *trans*-**7** in 72% yield. The acid hydrolysis results of both of *trans*-**5** and *cis*-**5** to the corresponding disulfoxides (*trans*-**7** and *cis*-**7**) suggest that the hydrolysis of S–NH to S–O proceeds preferentially through an inversion mechanism (ca. inversion %: 86% for *trans*-**5** to *cis*-**7**, and 89% for *cis*-**5** to *trans*-**7**, respectively). These results are in contrast to those found for the thermodynamically equilibrated mixture of *trans*-**5** and *cis*-**5** formed from the hydrolysis of *trans*-**2** *or* *cis*-**2** in concentrated H_2SO_4. Evidently the hydrolysis of **5** to **7** (the substitution of NH group by H_2O) is faster than the oxygen exchange on the sulfur atom of *trans*-**5** and *cis*-**5**, contrary to the result in concentrated H_2SO_4 as mentioned earlier. The decrease of the stereospecificity on the hydrolysis in aqueous H_2SO_4 is due mainly to the concurrent oxygen exchange reaction of the starting **5** and/or **7** initially formed. These results suggest that in a weak acid, such as 20% H_2SO_4, the aminosulfonium salt would be preferentially formed over the hydroxysulfonium salt and be followed by substitution with H_2O after further protonation of the nitrogen atom.

Thermal *cis*–*trans* isomerization of 10-monoxy-iminothianthrenes and thianthrene-5,10-dioxide: Another interesting aspect of the stereochemical reaction of iminothianthrene and sulfoxide derivatives is the thermal *cis*–*trans* interconversion. Optically active sulfilimines are known to be substantially thermally racemized by pyramidal inversion around 100 °C,[16] while racemization of sulfoxides takes place at higher temperatures.[17] We conducted a preliminary study on the thermal isomerization of the iminothianthrene derivatives; *trans*-**2** to *cis*-**2**, and *trans*-**5** to *cis*-**5**, and vice versa. *trans*-10-Monoxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (*trans*-**2**), when heated at 100 °C for 4.5 h, was found to undergo a 87% inversion at the sulfur atom bearing the NTs group, affording *cis*-**2** together with 10% recovery of *trans*-**2**. This ratio was found to be constant even after prolonged heating. Conversely, heating *cis*-**2** under the same conditions gave *trans*-**2** in 11% yield after equilibration. Upon heating *trans*-**5** under similar conditions, *cis*-**5** was obtained in 85% yield after equilibration, but *trans*-**5** was not recovered at all. When *cis*-**5** was heated under the same conditions, *cis*-**5** was recovered in 86% yield. However, in this reverse route *trans*-**5** was also not detected. In both cases, *trans*-**5** decomposed to thianthrene monoxide owing to the thermal de-imination reaction.[4] The instability of *trans*-**5** compared with *cis*-**5** may be due to the *trans*-annular interaction between the oxygen and the NH group. For a comparison with the results of thermal behavior of *trans*-**2**, *cis*-**2**, *trans*-**5**, and *cis*-**5**, thermal isomerization of *trans*-**7** to *cis*-**7**, and vice versa, was studied. The thermal equilibration of *trans*-**7** at 180 °C was found to undergo 80% thermal inversion of the sulfoxide affording *cis*-**7**, and *trans*-**7** was recovered in a 19% yield. Conversely, starting with *cis*-**7**, *trans*-**7** was formed in 18% yield with a 79% recovery of *cis*-**7**. These results, as summarized in Scheme 2, clearly indicate that the disulfoxides undergo thermal pyramidal inversion more slowly than the corresponding 10-monoxy-5-iminothianthrene derivatives *trans*-**5** and *cis*-**5**, and that the *cis*-thianthrene derivatives, that is, *cis*-**2**, *cis*-**5**, and *cis*-**7**, are thermodynamically more stable than the *trans* forms. Hydrolysis of *trans*-**2** and *cis*-**2** to the corresponding *N*-unsubstituted-sulfilimines in concentrated H_2SO_4 is also summarized in Scheme 2, together with the chemical conversion of *trans*-**5** to *trans*-**2** and *cis*-**5** to *cis*-**2** by *N*-tosylation of the corresponding *N*-unsubstituted-sulfilimines.

Conclusion

In the course of the study of thianthrene derivatives with a regulation functionality of their "flip-flap" motion for a development of a new class of functionalized materials, we preliminarily investigated the *cis*–*trans* isomerization of several 5,10-disubstituted thianthrene derivatives. The *trans*- or *cis*-10-monoxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (*trans*-**2** or *cis*-**2**) was hydrolyzed to a mixture of the *trans*-**5** and *cis*-**5** in concentrated H_2SO_4; this resulted in the preferential formation of the *cis* form and almost the same respective ratio (ca. 5:1) of a mixture of *trans*-**5** and *cis*-**5**. In 20% aqueous H_2SO_4 the hydrolysis reaction of *trans*-**5** or *cis*-**5** led to a mixture of the corresponding disulfoxides **7**, indicating that substitution of the NH group with H_2O proceeds through inversion (ca. 86–89%). In both cases the mechanistic aspect was discussed in view of the concurrent oxygen exchange reaction in H_2SO_4. Another interesting stereochemical problem concerning the thermal *cis*–*trans* interconversion of **2**, **5** and **7** was studied. In this case the *cis* derivatives were preferentially formed. The final structural confirmation of *trans*-**2**, *cis*-**2**, **3**, and *trans*-**5** was performed by X-ray crystallographic analyses, of which compound *trans*-**5** is a first example among *N*-unsubstituted-sulfilimines. From the results of the X-ray analysis, the relationship between the IR stretching frequencies and the bond lengths of S–O and S–N at the equatorial or axial conformational position was also discussed.

Experimental Section

All the melting points were uncorrected. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ with TMS as an internal standard. The mass spectra were recorded with an EI ($Ea = 70$ eV) ionization method. The Microanalytical Laboratory of the Department of Chemical and Biochemical Engineering of Toyama University performed the elemental analyses. All the reactions were monitored by TLC by using Merck Silica Gel 60 F_{254} TLC plates, and the products were separated by

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column chromatography using Merck Silica Gel 60 and also by preparative layer chromatography using Merck Silica Gel 60 PF_{254} with UV detection. All the reagents were of the highest quality and were further purified by distillation or recrystallization. Solvents were further purified by general methods.

5-(*N*-*p*-Toluenesulfonyl)iminothianthrene (1): The preparation procedure of *N*-*p*-toluenesulfonyliminothianthrenes is usually performed by the reaction of sulfides with chloramine T in a protic solvent, such as acetic acid or alcoholic solvents.[18] However, the best results were obtained using CH_3CN as a solvent, and by using chloramine T recrystallized from the same solvent. A mixture of thianthrene (3.5 g, 16 mmol) and chloramine T trihydrate (6.94 g, 24 mmol) in CH_3CN (100 mL) was stirred amd hested to reflux for 3.5 h. After the solvent was removed, the residue was washed with H_2O and diethyl ether to afford 5.4 g (87 % yield) of almost pure 5-(*N*-p-toluenesulfonyl)iminothianthrene (**1**). Recrystallization from CH_3CN gave a pure compound: m.p. 174–175 °C (CH_3CN); lit. m.p. 168–169 °C;[18a] ^{1}H NMR: $\delta = 2.40$ (s, 3H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.45–7.52 (m, 4H), 7.64–7.66 (m, 2H), 7.89–7.92 (m, 2H), 7.94 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR: $\delta = 21.5$, 125.7, 126.3, 129.0, 129.47, 129.49, 130.2, 131.0, 134.1, 140.9, 142.2; IR (KBr): $\tilde{\nu} = 1305$, 1140, 960 cm^{-1}.

Oxidation of 5-(*N*-*p*-toluenesulfonyl)iminothianthrene (1) with *m*-CPBA: Compound **1** (3.0 g, 7.8 mmol) was dissolved in CH_2Cl_2 (30 mL). *m*-CPBA (1.77 g, 10.2 mmol) in CH_2Cl_2 (31 mL) was added to this solution. The solution was stirred at RT until the TLC spot of the starting sulfilimine disappeared. The solution was washed with 3 % aqueous NaOH and H_2O, and dried over anhydrous $MgSO_4$. After the solvent was removed, the residue was chromatographed (EtOAc/$CHCl_3$ = 1:1) through a column packed with silica gel to afford *trans*-10-monoxy- (*trans*-**2**, 2.29 g, 73 %) and 10-dioxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (**3**, 0.7 g, 21 %), which were recrystallized from dichloromethane–hexane and acetonitrile, respectively.

Compound *trans*-2: M.p. 210–215 °C;[20] ^{1}H NMR: $\delta = 2.37$ (s, 3H), 7.20 (d, $J = 8.3$ Hz, 2H), 7.61–7.65 (m, 2H), 7.68–7.72 (m, 2H), 7.77 (d, $J = 8.3$ Hz, 2H), 8.02–8.05 (m, 2H), 8.06–8.08 (m, 2H); ^{13}C NMR: $\delta = 21.4$, 126.2, 128.3, 129.0, 129.4, 131.8, 132.4, 132.9, 140.5, 142.2, 143.8; IR (KBr): $\tilde{\nu} =$ 1290, 1140, 1080, 920 cm^{-1}; MS (EI): *m/z* (%): 401 $[M]^+$; elemental analysis calcd (%) for $C_{19}H_{15}NO_3S_3$: C 56.84, H 3.77, N 3.49; found C 56.76, H 3.75, N 3.54.

Compound 3: M.p. 250–252 °C; ^{1}H NMR: $\delta = 2.44$ (s, 3H), 7.33 (d, $J =$ 8.3 Hz, 2H), 7.71–7.78 (m, 4H), 7.98 (d, $J = 8.3$ Hz, 2H), 8.07–8.11 (m, 2H), 8.16–8.20 (m, 2H); ^{13}C NMR: $\delta = 21.5$, 126.42, 126.45, 126.5, 129.8, 131.8, 133.5, 135.2, 139.3, 140.2, 143.0; IR (KBr): $\tilde{\nu} = 1320$, 1160, 960 cm^{-1}; MS (EI): *m/z* (%): 417 $[M]^+$; elemental analysis calcd (%) for $C_{19}H_{15}NO_4S_3$: C 54.66, H 3.62, N 3.35; found C 54.92, H 3.51, N 3.41.

General procedure for acidic hydrolysis of 5-(*N*-*p*-toluenesulfonyl)iminothianthrenes *trans*-2, *cis*-2, and 3, to their iminothianthrenes *trans*-5, *cis*-5, and 4: 5-(*N*-*p*-Toluenesulfonyl)iminothianthrene *trans*-**2**, *cis*-**2**, or **3** (2.2–2.52 mmol) was dissolved in of H_2SO_4 (4 mL, commercial; 95 %) at RT. After 30 min., the solution was poured onto ice, made basic with aqueous KOH, and extracted with $CHCl_3$. The solvent was removed under reduced pressure and the residue dissolved in 3 % aqueous H_2SO_4, followed by extraction with three small portions of $CHCl_3$ (5 mL) to remove undesired neutral and acidic materials. The solution was made basic again with aqueous KOH and extracted thoroughly with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O and dried over anhydrous $MgSO_4$. Then the solvent was removed to afford crude 5-iminothianthrene *trans*-**5**, *cis*-**5**, or **4**. Purification by column chromatography on silica gel (EtOAc/C_6H_{14} = 2:1) or by recrystallization from CH_2Cl_2/C_6H_{14} yielded the pure *N*-unsubstituted sulfilimine, *trans*-**5**, *cis*-**5**, or **4** as described below.

***trans*-10-Monoxy-5-iminothianthrene (*trans*-5) and *cis*-10-monoxy-5-iminothianthrene (*cis*-5b)**: a) Starting from the *trans*-**2** (1.01 g, 2.52 mmol), a mixture of *trans*- and *cis*-**5** (0.54 g) was obtained in 87 % yield as a colorless crystalline material, whose *trans*-*cis* = ratio (74:13) was directly determined by ^{1}H NMR spectroscopy. b) Starting from the *cis*-**2** (1.00 g, 2.49 mmol), a mixture of *trans*- and *cis*-**5** (0.57 g) was obtained in 92 % yield as a colorless crystalline material, whose *trans*-*cis* ratio (77:15) was directly determined by ^{1}H NMR spectroscopy. These two routes resulted in providing almost the same *trans*/*cis* ratio for the mixture of products *trans*- and *cis*-**5**. Pure *trans*-**5** was obtained by several recrystallizations from CH_2Cl_2/C_6H_{14}. Pure *cis*-**5** was directly obtained by chromatography on silica gel or by the thermal pyramidal isomerization of *trans*-**5** as described later in the Experimental Section.

Compound *trans*-5: M.p. 252–259 °C (decomp); ^{1}H NMR: $\delta = 1.66$ (s, 1H), 7.57–7.61 (m, 2H), 7.70–7.74 (m, 2H), 7.94–7.96 (m, 2H), 8.33–8.35 (m, 2H); ^{13}C NMR; $\delta = 126.5$, 129.2, 130.2, 132.3, 139.3, 146.1; IR (KBr): $\tilde{\nu} =$ 3190, 1010, 930 cm^{-1}; MS (EI): *m/z* (%): 247 $[M]^+$; elemental analysis calcd (%) for $C_{12}H_9NOS_2$: C 58.27, H 3.66, N 5.66; found C 58.40, H 3.45, N 5.65.

Compound *cis*-5: M.p. 233–239 °C (decomp); ^{1}H NMR: $\delta = 1.26$ (s, 1H), 7.67–7.73 (m, 4H), 8.02–8.06 (m, 2H), 8.14–8.19 (m, 2H); ^{13}C NMR: $\delta =$ 123.4, 123.9, 130.4, 130.7, 138.4, 139.4; IR (KBr): $\tilde{\nu} = 3200$, 1070, 935 cm^{-1}; MS (EI); *m/z* (%): 247 $[M]^+$; elemental analysis calcd (%) for $C_{12}H_9NOS_2$: C 58.27, H 3.66, N 5.66; found C 57.97, H 3.69, N 5.71.

10-Dioxy-5-iminothianthrene (4): Starting from **3** (0.92 g, 2.2 mmol), **4** was obtained as colorless crystalline material (0.52 g, 90 %) after recrystallization from CH_2Cl_2/C_6H_{14}. M.p. 195–201 °C (decomp); ^{1}H NMR: $\delta = 1.67$ (s, 1H), 7.66–7.70 (m, 2H), 7.76–7.80 (m, 2H), 8.15–8.17 (m, 2H), 8.26–8.28 (m, 2H); ^{13}C NMR; $\delta = 126.6$, 129.3, 132.3, 139.4, 130.2, 146.2; IR (KBr): $\tilde{\nu} = 3225$, 1310, 1160, 940 cm^{-1}; MS (EI): *m/z* (%): 263 $[M]^+$; elemental analysis calcd (%) for $C_{12}H_9NO_2S_2$: C 54.73, H 3.44, N 5.31; found C 54.59, H 3.13, N 5.33.

General procedure for the tosylation of iminothianthrenes 4, *trans*-5, and *cis*-5: Tosyl chloride (47.6 mg, 0.25 mmol) in CH_2Cl_2 (3 mL) was added to 5-*N*-iminothianthrene **4**, *trans*-**5**, or *cis*-**5** (ca. 0.20 mmol) and triethylamine (34 μL, 0.25 mmol) in CH_2Cl_2 (6 mL) at RT. After 1 h of stirring, the reaction mixture was washed with H_2O and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by either preparative layer chromatography (silica gel; EtOAc/$CHCl_3$ = 1:1) or column chromatography on silica gel (EtOAc/$CHCl_3$ = 1:2) to afford 5-(*N*-*p*-toluenesulfonyl)iminothianthrenes **3**, *trans*-**2**, or *cis*-**2**, as confirmed by their m.p., and ^{1}H NMR and IR spectra.

10-Dioxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (3): Starting from **4** (50.3 mg, 0.19 mmol), **3** was obtained as colorless solid (72.9 mg, 91 %) after preparative layer chromatography and purified by crystallization from CH_3CN.

***trans*-10-Monoxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (*trans*-2)**: Starting from *trans*-**5** (49.8 mg, 0.20 mmol), *trans*-**2** was obtained as colorless crystals (71.0 mg, 88 %) after crystallization from CH_2Cl_2/C_6H_{14}.

***cis*-10-Monoxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (*cis*-2)**: Starting from *cis*-**5** (49.9 mg, 0.20 mmol), *cis*-**2** was obtained as fine colorless crystals (69.4 mg, 86 %) after recrystallization from a mixture of CH_2Cl_2/C_6H_{14}. M.p. 215–221 °C (thermal pyramidal inversion occurred, *cis*-**2** to *trans*-**2**);[19] ^{1}H NMR: $\delta = 2.43$ (s, 3H), 7.33 (d, $J = 8.5$ Hz, 2H), 7.66–7.70 (m, 2H), 7.75–7.79 (m, 2H), 7.97 (d, $J = 8.5$ Hz, 2H), 8.02–8.04 (m, 2H), 8.06–8.08 (m, 2H); ^{13}C NMR: $\delta = 21.5$, 124.3, 124.9, 126.4, 129.2, 129.7, 131.4, 131.9, 139.2, 140.4, 142.8; IR (KBr): $\tilde{\nu} = 1290$, 1140, 1080, 1000 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{15}NO_3S_3$: C 56.84, H 3.77, N 3.49; found C 56.85, H 3.73, N 3.47.

General procedure for the conversion of S–NH to a S–O group in 5-iminothianthrenes 4, *trans*-5, or *cis*-5 under aqueous acidic conditions: 5-(*N*-*p*-Toluenesulfonyl)iminothianthrenes **4**, *trans*-**5**, or *cis*-**5** (ca. 0.20 mmol) was dissolved in 5 mL of 20 % aqueous H_2SO_4, heated to 65 °C and stirred for 3 h, cooled to RT, and thoroughly extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O and dried over anhydrous $MgSO_4$. The solvent was removed affording the corresponding thianthrene oxides **6**, *trans*-**7**, or *cis*-**7**, which were purified by either recrystallization from CH_2Cl_2/C_6H_{14} or preparative layer chromatography on silica gel (EtOAc/$CHCl_3$ = 1:1) followed by recrystallization from EtOAc/C_6H_{14}.

Thianthrene-5,5,10-trioxide (6): Starting from compound **4** (50.3 mg, 0.19 mmol) compound **6** was recrystallized from CH_2Cl_2/C_6H_{14} as colorless crystals (48.2 mg, 95 %). Characterization was confirmed by comparison with the m.p., IR, and NMR data of an authentic sample prepared by a known method[11] and also with data reported in the literature:[7] m.p. 223–224 °C; ^{1}H NMR: $\delta = 7.69–7.73$ (m, 2H), 7.76–7.80 (m, 2H), 8.13–8.17 (m, 4H); ^{13}C NMR: $\delta = 125.0$, 126.0, 130.7, 133.0, 134.1, 147.7; IR (KBr): $\tilde{\nu} =$ 1315, 1160, 1075 cm^{-1}.

***trans*-Thianthrene-5,10-dioxide (*trans*-7) and *cis*-thianthrene-5,10-dioxide (*cis*-7)**: a) Starting from *trans*-**5** (50.0 mg, 0.20 mmol), a mixture of *trans*- and *cis*-thianthrene-5,10-dioxide, (*trans*- and *cis*-**7**) was obtained in 12 and 73 % yield, respectively, as a colorless crystalline material after separation

of *trans*- and *cis*-**7** and purification by preparative layer chromatography on silica gel (EtOAc/$CHCl_3$ = 1:1) followed by recrystallization from EtOAc/C_6H_{14}. b) Starting from *cis*-**5** (50.2 mg, 0.20 mmol), a mixture of *trans*- and *cis*-thianthrene-5,10-dioxide (*trans*- and *cis*-**7**) was obtained in 72 and 10% yield as a colorless crystalline material, after the same separation procedure described above. The separated products showed the same m.p., IR, and ^{1}H NMR data as those of authentic *trans*- and *cis*-thianthrene-5,10-dioxides.[20, 21] *Trans*-**7**: m.p. 259–261 °C; ^{1}H NMR: δ = 7.64–7.69 (m, 4H), 8.08–8.13 (m, 4H); ^{13}C NMR: δ = 127.7, 131.4, 142.8; IR (KBr): $\tilde{\nu}$ = 1070, 1025 cm^{-1}. *Cis*-**7**: m.p. 289–295 °C; ^{1}H NMR: δ = 7.70–7.74 (m, 4H), 8.05–8.10 (m, 4H); ^{13}C NMR: δ = 123.7, 130.8, 138.3; IR (KBr): $\tilde{\nu}$ = 1090cm^{-1}.

General procedure for the thermal *cis*–*trans* isomerization in monoxy-5-imino, or -5-(*N*-*p*-toluenesulfonyl)iminothianthrenes (*trans*-2, *cis*-2, *trans*-5, or *cis*-5): A suspension of monoxy-5-(*N*-*p*-toluenesulfonyl)iminothianthrene (*trans*- *or cis*-**2**, ca. 0.25 mmol in 20 mL of toluene), was heated to 100 °C while stirring. The solution became homogeneous after ca. 20 min. After thermal equilibration (4.5 h, monitored by TLC and HPLC in the preliminary experiment), toluene was removed in vacuo, and the residue was then purified by preparative layer chromatography (silica gel; EtOAc/$CHCl_3$ = 1:1). In the case of *trans*- and *cis*-**5** (ca. 0.40 mmol in 20 mL toluene), the purification was achieved as follows. After removal of the solvent, the residue was dissolved in 3% aqueous H_2SO_4, followed by extraction with $CHCl_3$ to remove the undesired neutral and acidic materials, and then this solution was made basic with aqueous KOH and thoroughly extracted with $CHCl_3$, followed by the usual workup procedure.

Thermal *cis*-*trans* isomerization of *trans*- and *cis*-2: a After 4.5 h thermal equilibration and workup of *trans*-**2** (101 mg, 0.25 mmol in 20 mL of toluene), an equilibrium mixture of *trans*-**2** (10.0 mg, 10%) and *cis*-**2** (86.4 mg, 87%) was obtained and the compounds were identified by IR and ^{1}H NMR spectroscopy. b After 4.5 h equilibration and workup of *cis*-**2** (100.2 mg, 0.25 mmol) in toluene (20 mL), an equilibrium mixture of *trans*-**2** (11.2 mg, 11%) and *cis*-**2** (87.2 mg, 87%) was obtained and the compounds were identified by IR and ^{1}H NMR spectroscopy. Both routes resulted in almost the same *trans*–*cis* ratio for the mixture of products *trans*- and *cis*-**2**.

Thermal *cis*–*trans* isomerization of *trans*- and *cis*-5: a After 6 h equilibration and workup of *trans*-**5** (101 mg, 0.41 mmol in 40 mL of toluene), only *cis*-**5** (85.1 mg, 85%) was detected and no other product. The compound was identified by IR and ^{1}H NMR spectroscopy. b After 6 h equilibration and workup of *cis*-**5** (101 mg, 0.41 mmol in 40 mL of toluene), only *cis*-**5** (87 mg, 86%) was detected, and no other product. The *cis*-**5** was identified by IR and ^{1}H NMR spectroscopy.

Thermal *cis*–*trans* isomerization of *cis*- and *trans*- thianthrene-5,10-dioxide (*trans*- and *cis*-7): A suspension of thianthrene-5,10-dioxide (*trans*- *or cis*-**7**) in *o*-dichlorobenzene (10 mL) was stirred and heated under reflux at 180 °C. After thermal equilibration (24 h, monitored by TLC and HPLC), the solvent was removed by bulb to bulb distillation, and the residue was purified by preparative layer chromatography (silica gel; EtOAc/$CHCl_3$ = 1:10). a After 24 h equilibration and workup of *trans*-**7** (50.5 mg, 0.225 mmol) an equilibrium mixture of *trans*-**7** (9.5 mg, 19%) and *cis*-**7** (40.6 mg, 80%) was obtained, and the compounds were identified by IR and ^{1}H NMR spectroscopy. b After 24 h equilibration and workup of *cis*-**7** (50.4 mg, 0.225 mmol), an equilibrium mixture of *trans*-**7** (9.1 mg, 18%) and *cis*-**7** (39.6 mg, 79%) was obtained, and the compounds were identified by IR and ^{1}H NMR spectroscopy. Both routes resulted in almost the same *trans*–*cis* ratio for the mixture of products of *trans*-**7** and *cis*-**7**.

X-ray crystallographic analysis of *trans*-2, *cis*-2, 3, and *trans*-5: Suitable crystals were mounted on top of a glass fiber with epoxy resin, and their respective X-ray data were collected on a Mac Science DIP2000 four-circle diffractometer with graphite-monochromatic $Mo_{K\alpha}$ radiation (λ = 0.71073) by using the $\omega/2\theta$ scan technique. All data ($2\theta_{max} = 50°$) were corrected for Lorenz and polarisation effects, but not for crystal absorption. The respective structures were solved by using direct methods[22] and refined on F^2 by full-matrix least-squares techniques for data with $F_o^2 > 3.00\sigma(F_o^2)$, and using the weighting scheme, $w = (\exp(10\sin(\theta)^2/\lambda^2))/(\sigma F_o)^2$. Non-hydrogen atoms were modeled anisotropically with neutral atom scattering factors.[23] Hydrogen atoms were initially added at calculated positions and allowed to refine isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134062–134065, for *trans*-**2**, *cis*-**2**, **3**, and *trans*-**5**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Compound *trans*-2: $C_{19}H_{15}NO_3S_3$; colorless prismatic crystal ($0.20 \times 0.33 \times 0.40$ mm^3); triclinic; space group: $P\bar{1}$; a = 6.993(1) Å, b = 8.028(1) Å, c = 16.622(1) Å, α = 100.675(4)°, β = 94.844(4)°, γ = 88.856(4)°, V = 913.11(5) Å^3, Z = 2, ρ_{calcd} = 1.29 g cm^{-3}, μ = 4.077 cm^{-1}. The final cycle of least-squares refinement based on 2851 unique reflections and 295 variable parameters converged with R = 0.045 and wR = 0.054. The residual electron density features in the final difference Fourier map are in the range from 0.47 to −0.27 e Å^{-3}.

Compound *cis*-2: $C_{19}H_{15}NO_3S_3$; colorless prismatic crystal ($0.20 \times 0.20 \times 0.30$ mm^3); triclinic; space group: $P\bar{1}$; a = 6.703(1) Å, b = 8.212(1) Å, c = 16.431(1) Å, α = 94.663(4)°, β = 95.849(4)°, γ = 93.794(4)°, V = 894.49(8) Å^3, Z = 2, ρ_{calcd} = 1.37 g cm^{-3}, μ = 5.235 cm^{-1}. The final cycle of least-squares refinement based on 2769 unique reflections and 286 variable parameters converged with R = 0.040 and wR = 0.047. Only the methyl hydrogen coordinates were not refined. The residual electron density features in the final difference Fourier map is in the range from 0.35 to −0.37 e Å^{-3}.

Compound 3: $C_{19}H_{15}NO_4S_3$; colorless crystal ($0.15 \times 0.20 \times 0.35$ mm^3); monoclinic; space group: $P2_1/n$; a = 11.112(1) Å, b = 11.853(1) Å, c = 14.622(1) Å, β = 91.029(4)°, V = 913.11(5) Å^3, Z = 4, ρ_{calcd} = 1.38 g cm^{-3}, μ = 3.916 cm^{-1}. The final cycle of least-squares refinement based on 2932 unique reflections and 304 variable parameters converged with R = 0.037 and wR = 0.045, with residual electron density in the range from 0.29 to −0.33 e Å^{-3}.

Compound *trans*-5: $C_{12}H_9NOS_2$; colorless crystal ($0.15 \times 0.20 \times 0.35$ mm^3); orthorhombic; spce group: $Pcmn$; a = 6.593(1) Å, b = 11.323(1) Å, c = 14.040(1) Å, V = 9.13.11(5) Å^3, Z = 4, ρ_{calcd} = 1.56 g cm^{-3}, μ = 4.550 cm^{-1}. The final cycle of least-squares refinement based on 943 unique reflections and 98 variable parameters converged with R = 0.038 and wR = 0.043, with residual electron density in the range from 0.76 to −0.31 e Å^{-3}.

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