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# Sterically Overcrowded Alkenes; Synthesis, Resolution and Circular Dichroism Studies of Substituted Bithioxanthylidenes#

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**Abstract**: Bithioxanthylidenes with small substituents at positions 2 and 2' have been synthesized and resolved by chiral HPLC. The X-ray molecular structure of 9-(2'-methyl-9'H-thioxanthene-9'-ylidene)-9H-xanthene (**17**) confirms the folded form of these molecules. UV and CD studies of several bithioxanthylidenes are presented. The CD spectra of these molecules can be described qualitatively by subtracting the CD spectra of both differently sensed helices (M and P) present in the molecule, which can be distinguished by the substituents at positions 2 and 2'.

## Introduction

Sterically overcrowded ethylenes have attracted considerable attention due to their intriguing conformational behaviour.[1] The chirality of disubstituted bistricyclic alkenes was demonstrated by extended $^1$H NMR investigations of disubstituted biacridanes,[2] bixanthylidenes,[3] bianthrones[4] and bifluorenylidenes[5] and for conformational interconversions energy barriers ($\Delta G^{\ddagger}$) ranging from 12-22 kcal.mol$^{-1}$ have been reported. No successful resolution into the enantiomers of these types of compounds was achieved so far. Recently, we reported the synthesis, resolution and stability towards thermal racemization of thioxanthene based bistricyclic alkenes.[6] A remarkable enhancement of the thermal stability was observed for these molecules, for instance, 2-methyl-9-(9'H-thioxanthene-9'-ylidene)-9H-thioxanthene (1, Figure 2) showed a racemization barrier $\Delta G^{\ddagger}$ of 27.3 kcal.mol$^{-1}$! Therefore these molecules could be resolved by chiral HPLC. Until now no CD spectra of bistricyclic dissymmetric alkenes have been published as far as we know, apart from a conformationally fixed bifluorenylidene.[5b] The geometry of this *twisted* bifluorenylidene molecule however deviates strongly from the *folded* bistricyclic alkenes described in this paper (vide infra).

#This paper is dedicated to the late Prof. Günther Snatzke.

Inherently dissymmetric alkenes[1] are very interesting molecules from the perspective of structural organic chemistry. These molecules lack a stereogenic center, but are chiral due to a non-planar, helical structure. The non-planarity is caused by steric interactions between the substituents attached to the central double bond.

In order to release steric strain in overcrowded alkenes two mechanisms are proposed, generally known as *folding* and *twisting* (Figure 1).[1]

In a folded structure the tricyclic moieties at both ends of the central olefinic bond are folded in opposite directions. This can be achieved by rotating around the four bonds attached to the ethylenic carbons, as is the case in most bistricyclic ethylenes.[7,8,9,10] The bond angles around the ethylenic carbons deviate strongly from 120° and in some cases pyramidalization occurs.[11] If all four substituents are equal a non-chiral centrosymmetric structure, pointgroup $C_{2h}$, will result. This is illustrated for bixanthylidene[8] in Figure 1. An important consequence is that folded bistricyclic alkenes can be chiral only if the symmetry is broken by the presence of one or more substituents. In the case of a disubstituted folded bistricyclic alkene bearing the same substituents on identical positions of both tricyclic systems, the cis isomer is *chiral* but the trans isomer is still a centrosymmetric *achiral* molecule ($S_2$ symmetry).

In a twisted structure both halves of the molecule, bisected by the central double bond, are either sterically very demanding[12] or planar and rigid,[13] mostly due to the presence of a five membered ring attached to the ethylenic carbons. For releasing steric strain a twist over the central double bond is inflicted, but both halves of the molecule remain planar. For bifluorenylidenes[13] the twist over the central double bond is 42°, but for benzannulated analogues a twist up to 70° has been proposed.[14] If all four substituents are equal, as illustrated by bifluorenylidene in Figure 1, the resulting structure exhibits $D_2$ symmetry. As a consequence twisted bistricyclic alkenes will always be chiral, apart from the case where the twist angle is 90°.

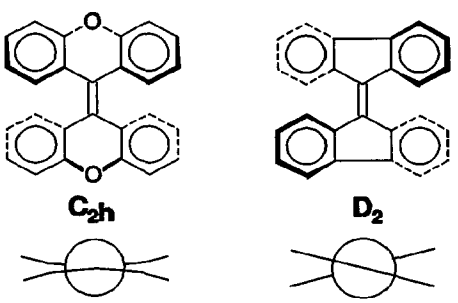
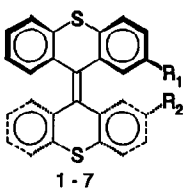



*Figure 1. A folded and a twisted bistricyclic alkene; schematic structure and projection along the central double bond.*

In this paper we report the synthesis and resolution of several mono- and disubstituted bithioxanthylidenes. Furthermore we describe the CD data of these compounds being the first CD study of folded inherent dissymmetric sterically overcrowded (bistricyclic) alkenes.

**Synthesis**

In order to study the resolution and chiroptical properties of substituted bithioxanthylidenes, 2-methyl-9-(9'H-thioxanthene-9'-ylidene)-9H-thioxanthene (**1**) and several 2,2'-disubstituted bithioxanthylidenes **2** - **7** were synthesized (Figure 2).

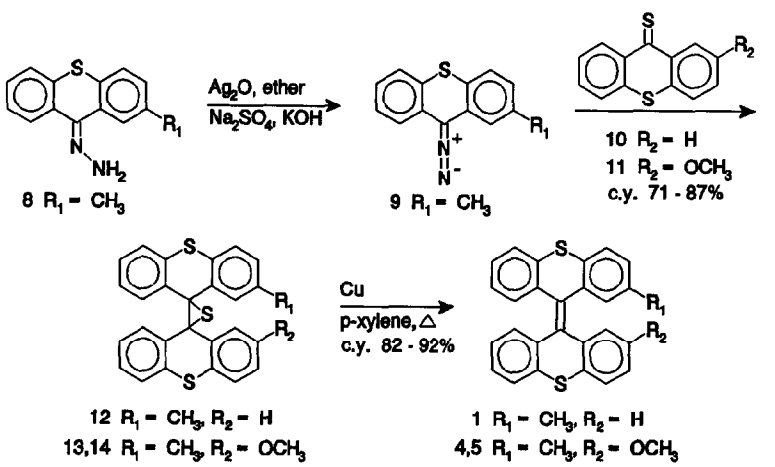



1 - 7

*Figure 2. Bithioxanthylidenes 1 - 7*

| compound | $R_1$ | $R_2$ |
|---|---|---|
| **1** | $CH_3$ | H |
| *cis*-**2** | $CH_3$ | $CH_3$ |
| *trans*-**3** | $CH_3$ | $CH_3$ |
| *cis*-**4** | $CH_3$ | $OCH_3$ |
| *trans*-**5** | $CH_3$ | $OCH_3$ |
| *cis*-**6** | $OCH_3$ | $OCH_3$ |
| *trans*-**7** | $OCH_3$ | $OCH_3$ |

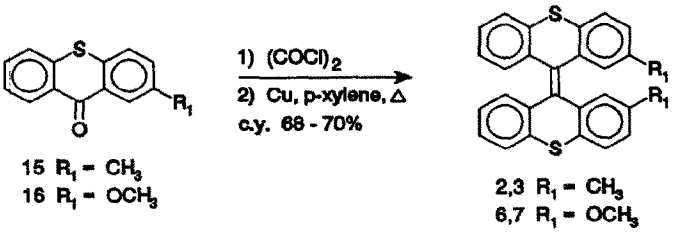
The synthesis of bithioxanthylidenes **1**, *cis*-**4** and *trans*-**5**, containing different substituents in the upper and lower halves, is shown in Scheme 1 and is based on the diazo-thioketone cycloaddition[15,16] as a key step to form the sterically demanding central double bond. Hydrazone **8** was prepared from 4-iodotoluene whereas thione **11** was obtained from 4-iodoanisole in analogy to reported procedures.[17]




*Scheme 1. Synthesis of alkenes 1, cis-4 and trans-5*

Oxidation of **8** to diazo compound **9** followed by addition of **10** or **11** provided episulfides **12**, *cis*-**13** and *trans*-**14**, respectively. Subsequent sulfur extrusion using copper powder in boiling p-xylene afforded bithioxanthylidenes **1**, **4** and **5** in high yields. A mixture of *cis*-**4** and *trans*-**5** isomers (50:50 ratio) was obtained in the latter case.

For the synthesis of bithioxanthylidenes **2**, **3**, **6** and **7** a coupling procedure via the corresponding 9,9-dichlorides was followed.[18] This method when applied in the formation of non-symmetrically substituted bithioxanthylidenes (vide supra) would provide mixtures of homo-coupled and cross-coupled products. Treatment of thioxanthenones **15** or **16** with oxalyl chloride provided the corresponding 9,9-dichlorides, which was followed by a coupling reaction with copper in boiling p-xylene to furnish **2**, **3**, **6** and **7**. Mixtures of *cis*-**2** and *trans*-**3** (58:42 ratio) and *cis*-**6** and *trans*-**7** (38:62 ratio) were obtained.




**15** $R_1 = CH_3$
**16** $R_1 = OCH_3$

**2,3** $R_1 = CH_3$
**6,7** $R_1 = OCH_3$

*Scheme 2. Synthesis of alkenes cis-2, trans-3, cis-6 and trans-7*

**Resolution**

Unfunctionalized chiral aromatic compounds can, in principle, be resolved by means of chiral HPLC.[19] We have previously shown the resolution of inherently dissymmetric sterically overcrowded alkenes by HPLC.[6,20,21,22] Using (+)-poly(triphenylmethyl)methacrylate[23] as a chiral stationary phase all *chiral* - mono-substituted as well as disubstituted- bithioxanthylidenes, depicted in Figure 2, could be resolved. For **1** two fractions were collected and for cis-trans mixtures of symmetrically substituted alkenes (**2/3** or **6/7**) three fractions were isolated. Of these three fractions the middle one was CD inactive while the first and third fractions showed identical CD spectra, apart from the sign of $\Delta\epsilon$. On basis of these observations we could assign the trans configuration to the second and the cis configuration to isomers from the first and third fractions. From a racemic mixture of **4** and **5** all four stereoisomers could be obtained. Two pairs of identical CD spectra (except for the sign) were obtained for the first and fourth and the second and third fractions, corresponding with the enantiomers of *cis*-**4** and *trans*-**5**, respectively. This assignment was based on the relative weak CD signal for the trans isomers (vide infra) and on comparison of the chromatographic behaviour of *trans*-**3** and *trans*-**7**. The chromatographic results are summarized in Table 1.

Table 1. Retention times ($t_1$, $t_2$, min) and separation factors ($\alpha$) of 1 - 7 on a (+)-poly(triphenylmethyl)methacrylate column using n-hexane/isopropanol 9:1 as eluent.

| compound | $t_1$ | $t_2$ | $\alpha$ | compound | $t_1$ | $t_2$ | $\alpha$ |
|---|---|---|---|---|---|---|---|
| **1** | 8.3 | 12.1 | 1.8 | | | | |
| **2** | 6.2 | 14.4 | 3.9 | **3** | 10.0 | | |
| **4** | 7.7 | 16.2 | 2.9 | **5** | 10.9 | 14.7 | 1.5 |
| **6** | 10.4 | 17.0 | 1.9 | **7** | 15.0 | | |

For the 2-methyl-2'-methoxy-bithioxanthylidenes (**4** and **5**) the best resolution was achieved for the cis isomers. From the CD spectra it appeared that all first eluted cis isomers have the same absolute configuration. From Table 1 it is also clear that better resolutions are achieved with methyl substituted bithioxanthylidenes despite the fact that the methoxy substituted alkenes have a stronger interaction with the column material. It is remarkable that separation of all four isomers of racemic cis-trans mixtures can be achieved and that relatively small substituents exert a large effect on the interaction of these inherent dissymmetric alkenes with (+)-poly(triphenylmethyl)methacrylate.

**X-Ray structure of a folded 2-substituted bistricyclic alkene**

In order to establish the expected folded structure and to obtain information about the influence of a substituent at position 2 on the structure of bistricyclic alkenes, an X-ray analyses of bithioxanthylidenes **1** - **7** seems to be highly warranted. Until now X-ray structures of bithioxanthylidenes have not been published and, unfortunately, no crystals of **1** - **7** suitable for X-ray analysis could be obtained. Therefore, an X-ray analysis of 9-(2'-methyl-9'H-thioxanthene-9'-ylidene)-9H-xanthene (**17**)[6] was performed. Crystallization from absolute ethanol afforded **17** as small white crystals suitable for X-ray analysis. The molecular structure of **17** including the adopted numbering scheme is depicted in Figure 3. Some selected bond lengths, bond angles and dihedral angles are given in Table 2.

We will describe this structure in some detail since **17** is structurally closely related to the bithioxanthylidenes **1** - **7** and might give us information on the influence of the methyl substituent on the basic structure of the alkene.[24]

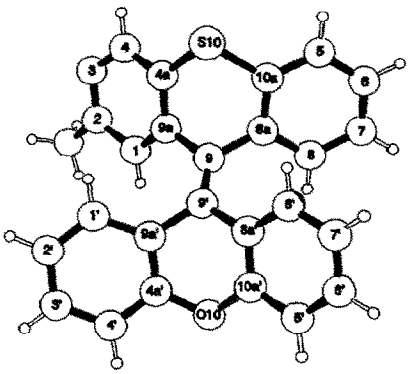



*Figure 3. X-ray structure of 9-(2'-methyl-9'H-thioxanthene-9'-ylidene)-9H-xanthene (17).*

Table 2. Selected bond lengths (Å), bond angles (°) and dihedral angles (°) for **17**.*

| | | | |
|---|---|---|---|
| **Bond lengths.** | | | |
| $C_9$-$C_{9'}$ | 1.33(2) | | |
| $S_{10}$-$C_{10a}$ | 1.77(1) | $S_{10}$-$C_{4a}$ | 1.75(1) |
| $O_{10'}$-$C_{10a'}$ | 1.38(1) | $O_{10'}$-$C_{4a'}$ | 1.38(1) |
| $C_4$-$C_{4a}$ | 1.36(2) | $C_5$-$C_{10a}$ | 1.41(1) |
| $C_{4'}$-$C_{4a'}$ | 1.38(2) | $C_{5'}$-$C_{10a'}$ | 1.40(2) |
| **Bond angles.** | | | |
| $C_{9a}$-$C_9$-$C_{8a}$ | 112(2) | $C_{9a'}$-$C_{9'}$-$C_{8a'}$ | 110.1(8) |
| $C_{9a}$-$C_9$-$C_{9'}$ | 125.6(8) | $C_{9a'}$-$C_{9'}$-$C_9$ | 127(1) |
| $C_{8a}$-$C_9$-$C_{9'}$ | 123(2) | $C_{8a'}$-$C_{9'}$-$C_9$ | 123(1) |
| $C_{4a}$-$C_{9a}$-$C_9$ | 115.9(7) | $C_{10a}$-$C_{8a}$-$C_9$ | 120(2) |
| $C_1$-$C_{9a}$-$C_{4a}$ | 120.3(9) | $C_8$-$C_{8a}$-$C_{10a}$ | 117.2(2) |
| $C_2$-$C_1$-$C_{9a}$ | 119.1(9) | $C_7$-$C_8$-$C_{8a}$ | 124(1) |
| $C_{4a}$-$S_{10}$-$C_{10a}$ | 97.9(5) | $C_{4a'}$-$O_{10'}$-$C_{10a'}$ | 115.2(7) |
| **Dihedral angles.** | | | |
| $C_{9a}$-$C_9$-$C_{9'}$-$C_{9a'}$ | 5.82 (0.93) | $C_{9a}$-$C_9$-$C_{9'}$-$C_{8a'}$ | -177.25 (0.66) |
| $C_{8a}$-$C_9$-$C_{9'}$-$C_{8a'}$ | 3.71 (1.00) | $C_{8a}$-$C_9$-$C_{9'}$-$C_{9a'}$ | -173.22 (0.56) |
| $C_9$-$C_{9'}$-$C_{9a'}$-$C_{1'}$ | -37.87 (0.85) | $C_9$-$C_{9'}$-$C_{8a'}$-$C_{8'}$ | 39.94 (1.11) |
| $C_{9'}$-$C_9$-$C_{9a}$-$C_1$ | -53.04 (1.08) | $C_{9'}$-$C_9$-$C_{8a}$-$C_8$ | 52.44 (2.78) |

* Numbers in parentheses are estimated deviations in the least significant digits.

The X-ray structure of **17** clearly shows an anti-folded structure. This folding is best illustrated by the angles between the mean planes through the phenyl rings in each tricyclic unit. For the xanthene part an angle of 36° was measured, while for the thioxanthene unit an angle of 51° was found. These values are larger than those observed for isolated tricyclic aromatic systems apparently due to steric interactions between upper and lower halves. Both for bistricyclic alkenes[8,9,10] and tricyclic aromatic systems[25,26] increasing the size of the heteroatom at position 10 results in an increase of the angle between the phenyl rings.

Another feature common to the anti-folded bistricyclic alkenes is the strong deformation of the bond angles around $C_9$. For **17** $C_{9a'}$-$C_{9'}$-$C_{8a'}$ is decreased to 110° while the other two angles are increased to 127°! In general decreasing the size of the heteroatom at position 10 results in an increase in the deformation of the angles around $C_9$, as seen in **17**.

So far all structural features are analogous to those reported for anti-folded unsubstituted *achiral* bistricyclic alkenes.[7,8,9,10] Molecule **17** is *chiral* due to the presence of a symmetry breaking methyl group at position 2. It contains two helices of opposite sign; a M-helix containing a methyl substituent (left) and an unsubstituted P-helix.

The basic skeleton of the molecule is almost symmetrical but a close inspection reveals that some bond lengths and angles are not equal, for the right and left part of the molecule. Noteworthy are the differences between $C_4$-$C_{4a}$ and $C_5$-$C_{10a}$, and a 4° difference between $C_{9a'}$-$C_{9'}$-$C_9$ and $C_{8a'}$-$C_{9'}$-$C_9$. Close inspection of the central double bond shows that it is slightly twisted as illustrated by the Newman projection viewed along $C_9$-$C_{9'}$, as presented in Figure 4. The mean twist over the double bond is 4.8°. As far as we know this is the first example of an anti-folded bistricyclic alkene of which the central double bond is slightly twisted. It should be mentioned that this small twist makes the basic structure of the molecule chiral, and, apparently this twist is a consequence of the steric demands of the methyl substituent at $C_2$.[27]

Table 3. Bond angles of **17** viewed along $C_{9'}$-$C_9$ in degrees.

| | | | |
|---|---|---|---|
| $C_{8a}$-$C_{9a'}$ | 186.8 | $C_{9a}$-$C_{8a'}$ | 182.8 |
| $C_{8a}$-$C_{8a'}$ | 3.7 | $C_{9a}$-$C_{9a'}$ | 5.8 |
| $C_{9a}$-$C_{8a}$ | 179.0 | $C_{9a'}$-$C_{8a'}$ | 176.9 |

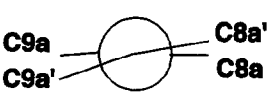



*Figure 4. Newman projection along $C_{9'}$-$C_9$*

**UV and CD studies**

The UV spectra of bithioxanthylidenes cannot adequately be described in terms of contributions of the individual thiophenol chromophores present in the molecules due to strong conjugation. To establish the extent of conjugation through the central double bond UV data of thioxanthene containing molecules are compared (Table 4).

Table 4. UV data of thioxanthene containing molecules in n-hexane.

| compound | $\lambda_{max}$/nm ($\epsilon$) | | | | | |
|---|---|---|---|---|---|---|
| thioxanthene | 210 s[a] (23250) | 225 s[a] (9180) | 252 s[a] (5850) | 266 (9500) | | |
| **12** | | 226 (37900) | 258 s[a] (16750) | 267 (18200) | 305 s[a] (4400) | |
| **1** | 206 (66000) | 239 (41000) | | 267 (17500) | 297 s[a] (11000) | 351(9800) |

[a]Shoulder.

For the thioxanthene part four different absorptions are present in the UV spectrum at 210 (s), 225 (s), 252 (s) and 266 nm. Calculations[28] have shown that these absorptions can be interpreted as being mainly due to sulfur to phenyl charge transfer transitions.

For episulfide **12** absorptions at 226, 258 (s), 267 and 305 nm (s) were observed. The appearance of the extra absorption at 305 nm is somewhat puzzling since no conjugation through the thiirane ring is expected. Interaction of the arene $\pi$-orbitals with sulfur d-orbitals might explain this additional absorption.

For alkene **1** absorptions at 206, 239, 267, 297 (s) and 351 nm were observed. Most of the bands present in the spectrum of the episulfide were also observed here. In addition an absorption appeared at 350 nm, apparently due to conjugation through the central double bond.

The UV spectra of bithioxanthylidenes **1** - **7** are very similar (for data, see Table 5) and illustrated by the spectrum of **1** in Figure 5. Since cis-trans mixtures could only be separated by chiral HPLC, the spectra presented for **2** - **7** were obtained from cis-trans mixtures. It should be noted that wavelengths of the absorption maxima are identical for cis and trans isomers. Based upon the UV data of pure *trans*-**7**,[29] we assume that the $\epsilon$ values are also identical for cis and trans isomers within this series.

As expected the methyl substituents hardly have any effect on the UV spectra whereas introduction of one or two methoxy substituents results in a bathochromic shift, especially for the long wavelength absorption.

Table 5. UV data of alkenes **1** - **7** in n-hexane.

| compound | $\lambda_{max}$/nm ($\epsilon$). | | | | |
|---|---|---|---|---|---|
| **1** | 206 (66000) | 239 (41000) | 267 (17500) | 297 s[a] (11000) | 351 (9800) |
| **2/3** | 204 (67600) | 235 (40500) | 264 (17600) | 297 (10800) | 350 (9500) |
| **4/5** | 218 (46000) | 235 (36000) | 268 (17500) | 300 s[a] (9700) | 359 (8700) |
| **6/7** | 212 (74900) | 234 (35000) | 267 (17800) | 300 s[a] (9500) | 365 (8600) |

[a]Shoulder.

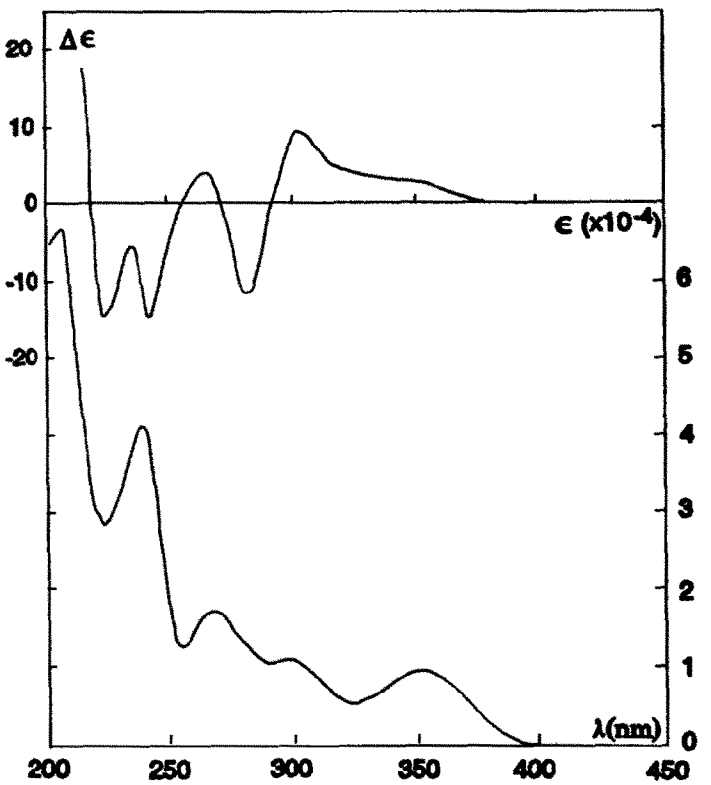



*Figure 5. UV and CD spectra of 1.*

The CD spectra of the bithioxanthylidenes are qualitatively similar except for that of **5**. The CD spectrum of (+) **1** shown in Figure 5 is illustrative. Above 220 nm five maxima are observed in the CD spectrum of **1**; 225 (-14.3), 244 (-14.6), 266 (3.8), 282 (-11.2), 303 (8.5) and 330 nm (shoulder, $\Delta\epsilon \approx 3.6$), see Table 6. The CD spectra of the cis and trans isomers **4** and **5** are presented in Figure 6.

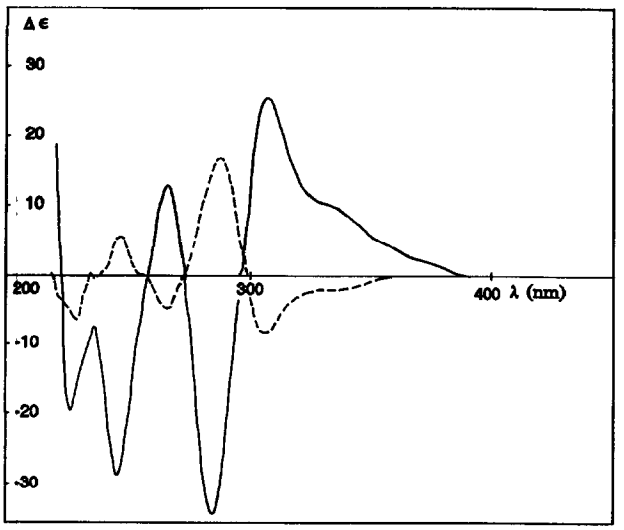



*Figure 6. CD spectra of 4 (solid line) and 5*

Table 6. CD spectra of alkenes **1**, **2** and **4** - **6** in n-hexane/isopropanol 9:1.

| compound | $\lambda_{max}$/nm ($\Delta\epsilon$) | | | | | |
|---|---|---|---|---|---|---|
| **1** | 225 (-14.3) | 244 (-14.6) | 266 (3.8) | 282 (-11.2) | 303 (8.5) | 330 s[a] (3.6) |
| **2** | 227 (-29.6) | 246 (-25.6) | 267 (6.6) | 284 (-18.0) | 304 (16.0) | 330 s[a] (9.3) |
| **4** | 226 (-18.4) | 247 (-27.4) | 267 (12.9) | 285 (-32.8) | 306 (24.8) | 335 s[a] (9.9) |
| **5** | 230 (-6.5) | 248 (5.9) | 267 (-4.7) | 288 (16.7) | 306 (-8.2) | 330 s[a] (-2.1) |
| **6**[b] | 227 (-21.1) | 247 (-21.3) | 267 (14.4) | 286 (-33.5) | 306 (22.8) | 335 s[a] (8.1) |

[a]Shoulder, [b]n-hexane as solvent.

After close inspection of the CD spectra of **1**, **2**, **4**, **5** and **6**, a number of features should be emphasized.

The low $\Delta\epsilon$ values found for these compounds, especially for alkenes **1** and **5** are striking. For other inherent dissymmetric alkenes, for instance the 1',2'-benzoannulated analogue of **1**, $\Delta\epsilon$ values up to 100 are reported.[22] Also in the CD spectra of inherent dissymmetric aromatic compounds containing phenyl chromophores such as cyclophanes,[30] biphenyls,[31,32] allenes[33] and others[34] significantly higher $\Delta\epsilon$ values than those of **1-6** are reported. An explanation for the small $\Delta\epsilon$ values of the *chiral* bithioxanthylidenes might be that these molecules do not deviate strongly from their *achiral* non-substituted analogues.

For methoxy containing compounds a small bathochromic shift is observed for almost all CD absorptions and for these compounds relatively intense absorptions are found at longer wavelengths

compared to their methyl analogues. Quantitatively the differences in CD spectra in this series of alkenes are substantial. For the disubstituted compounds **2** and **6** $\Delta\epsilon$ values twice as large as those for the monosubstituted compound **1** are observed.

For **1** the UV absorptions at 297 and 351 nm seem to correspond with positive CD absorptions at 303 and 330 nm. Apparently the 267 nm UV absorption gives rise to a bisignate pair of CD absorptions at 266 and 282 nm. The UV absorption at 239 nm might correspond to the bisignate CD absorptions at 225 and 244 nm. For the short wavelength absorption no correlation can be made yet. The same assignments can be made for the CD spectrum of **2**. For **4** and **6** roughly the same correlation can be made, however the long wavelength transitions at 359 and 365 nm, respectively, seem to be CD inactive.

From the observations made so far it is obvious that a simple determination of the absolute configuration by the exciton coupling method cannot be applied to these molecules.[35] The relative configuration of the molecules within this study can easily be determined because of the similarity of the CD spectra (except for **5**) and the elution order in the HPLC separation.

Furthermore, we propose a simple description of the spectra of substituted bithioxanthylidenes in terms of the CD spectra of monosubstituted bithioxanthylidenes. Therefore we must consider the bithioxanthylidenes as consisting of two opposite helices joined by the central double bond. Both helices will contribute to the observed CD spectrum and the CD spectrum of the whole molecule is roughly the sum of those of both helices. Subsequent introduction of substituents at positions 2 and 2' (or 7 and 7') will change the *molecular structure* and as long as small substituents are attached we expect their influence on the CD spectra to be additive. Therefore substitution at positions 7 and 7', the left P-helix in Figure 2, will make a positive contribution, while substituents at positions 2 and 2', at the right M-helix, will have a negative contribution. Both for the methyl and the methoxy groups we can determine the contribution from the CD spectra of **1**, **2** and **6**.
Using this model we might predict the CD spectra of a number of compounds bearing methyl or methoxy substituents at positions 2, 2', 7 or 7'.

For compounds bearing one type of substituent identical CD spectra for the monosubstituted and the trisubstituted compounds are expected and the CD spectrum of the 2,2'-disubstituted compounds will be twice as intense. All other isomers having equal numbers of substituents on both (opposite) helices will be CD inactive, a consequence of their symmetry.

Using two different substituents all isomers apart from a centro- and a sigma-symmetrical isomer will be chiral. If the contribution of the unequal substituents are in the same order of magnitude, as is the case for the methyl and methoxy substituents, we can expect CD spectra roughly

similar to those of their analogues bearing equal substituents (vide supra). Mono and trisubstituted isomers will have spectra roughly halve as intense as those of the 2,2'-disubstituted isomers. All other chiral isomers will have weak CD spectra reflecting the small difference between substituents.

Applying the rules just described the CD spectra of **1**, **2**, **4** and **5** were calculated (see Table 7). For compounds **1** and **2**, all bearing one type of substituent and the heterosubstituted compound **4**, reasonable correlations between calculated and experimental spectra were observed. From the spectra it is clear that for all these compounds the first eluted (+) enantiomers have the same relative configuration. For the heterosubstituted trans isomer **5** the calculated $\Delta\epsilon$ values are systematically too low, especially at longer wavelengths. But apart from the absorption at 248 nm both the position and the sign of the absorption maxima are well predicted. Therefore we can correlate its relative configuration to that of **1**, **2**, **4** and **6**. We can conclude that the helix bearing the methyl substituent in **5**, giving rise to relatively strong CD absorptions above 250 nm has the same helicity as the helices bearing methyl and methoxy substituents in **1**, **2**, **4** and **6**.

Table 7. Calculated CD spectra for **1**, **2**, **4** and **5**.

| Compound | $\lambda_{max}$/nm ($\Delta\epsilon$) | | | | |
|---|---|---|---|---|---|
| Me contrib[a] | 225 (-14.6) | 245 (-13.4) | 266 (3.5) | 283 (-9.7) | 303 (8.2) |
| MeO contrib[b] | 227 (-10.6) | 246 (-10.7) | 267 (7.2) | 286 (-16.8) | 306 (11.4) |
| calc **1** | 225 (-14.6) | 245 (-13.4) | 266 (3.5) | 283 (-9.7) | 303 (8.2) |
| calc **2** | 225 (-29.2) | 245 (-26.8) | 266 (7.0) | 283 (-19.4) | 303 (16.4) |
| calc **4** | 226 (-25.2) | 246 (-24.1) | 267 (10.7) | 285 (-26.5) | 304 (19.6) |
| calc **5** | 226 (-4.1) | 246 (-2.8) | 267 (-3.7) | 285 (7.0) | 304 (-3.2) |

[a] The methyl contribution was calculated by adding the CD spectra of **1** and **2** and dividing the resulting spectrum by 3. [b] The methoxy contribution was calculated by dividing the CD spectrum of **6** by 2.

**Conclusions.**

The effect of adding small substituents at positions 2, 2', 7 or 7' of bithioxanthylidenes on the intensity of their CD spectra seems to be additive and might be steric and electronic in nature. The possible role that steric interactions might play is shown by the X-ray structure of **17** in which a methyl group at position 2 induces a small twist over the central double bond. This twist will increase the pitch of the substituent bearing helix and reduce the pitch of the unsubstituted helix. It might be expected that the effect of more substituents will be additive as long as small twist angles are involved. Methyl and methoxy substituents are expected to induce comparable changes in geometry, since they are almost equal in size.[36]

Based on the UV spectra of **1** - **7**, electronic interactions are expected mainly to occur for the methoxy substituted alkenes. The influence of electronic changes in a chromophore on CD spectra of inherent dissymmetric aromatic compounds has been demonstrated by protonating or changing the orientation of pyridyl chromophores in [2.2] pyridinophanes.[37]

In conclusion we have successfully synthesized and resolved a number of chiral thermally stable bithioxanthylidenes, bearing small methyl and methoxy substituents at positions 2, 2', 7 or 7'. CD spectra of these compounds are presented and preliminary results show a simple correlation between the magnitude of the CD absorption and the substitution pattern. This allows us to determine the relative configuration of these compounds.

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*Experimental Section*

**General Methods**

Melting points (uncorrected) were determined on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope. $^1$H NMR spectra were recorded on a Varian VXR-300 spectrometer (at 300 MHz) using $CDCl_3$ as a solvent. Chemical shifts are denoted in $\delta$ units (ppm) relative to tetramethylsilane (TMS) as an internal standard at $\delta$ = 0.00 ppm. $^{13}$C NMR spectra were recorded on a Varian VXR-300 spectrometer (at 75.43 MHz) using $CDCl_3$ as solvent. The chemical shifts are denoted in $\delta$ units (ppm) with the solvent as an internal standard and converted to the TMS scale using $\delta$ ($CDCl_3$) = 76.91 ppm. High Resolution Mass Spectra (HRMS) were obtained on a AEI MS-902 spectrometer by Mr A. Kieviet. Elemental analyses were performed in the Microanalytical Department of the University of Groningen. The avarage values of duplo determinations are reported. CD spectra were taken on a Jobin Yvon Autodichrograph mark 5 and UV spectra on a Perkin Elmer lambda 5 UV\Vis spectrophotometer using n-hexane as solvent. HPLC separations were achieved using a 4.6*250 mm (+)-poly(triphenylmethyl) methacrylate column (DAICEL OT$^+$ from Daicel Chemical Industries) using n-hexane/isopropanol 9:1 as eluent (1 mL/min) at 10 °C. The X-ray analysis of **17** was performed by Mr. F van Bolhuis of the Crystal Structure Center in Groningen. All commercially available chemicals were obtained from Janssen Chimica or Aldrich and were used without further purification.

**Dispiro[2-methyl-9H-thioxanthene-9, 2'-thiirane-3', 9"-(9"H)-thioxanthene] (12)**
To a stirred solution of 2-methyl-9H-thioxanthene-9-one hydrazone (**8**, 720 mg, 3.0 mmol) in $Et_2O$ (40 mL) was added successively $Na_2SO_4$ (≈ 1.5 g), $Ag_2O$ (1.20 g, 5.0 mmol) and 5 drops of saturated KOH in methanol. The colour of the mixture rapidly turned violet and after 30 min the almost black solution of diazo compound **9** was filtered and the remaining residue washed with $Et_2O$ (10 mL). To this clear dark-purple solution was added 9H-thioxanthene-9-thione (**10**) in small portions. Evolution of nitrogen was observed and the deep purple colour disappeared. The thioketone (total amount 640 mg, 2.8 mmol) was added until the evolution of nitrogen had ceased and the colour of the solution had become light yellow. Episulfide **12** precipitated from the solution and was isolated by filtration to yield **12** as an analytically pure white powder (1.07 g, 2.4 mmol, 87.2%, based on the amount of added thioketone): mp 215.8-216.6 °C; $^1$H NMR (300 MHz) $\delta$ 2.18 (s, 3H), 6.74 (dd, $J$ = 7.3, 1.2 Hz, 1H), 6.92-7.25 (m, 10H), 7.46 (d, $J$ = 1.2 Hz, 1H), 7.65-7.69 (m, 3H); $^{13}$C NMR $\delta$ 20.87 (q), 60.01 (s, C-S), 61.82 (s, C-S), 122.93 (d), 123.21 (d), 123.35 (d), 123.36 (d), 124.58 (d), 124.68 (d), 126.51 (d), 126.52 (d), 126.55 (d), 126.82 (d), 127.40 (d), 128.42 (d), 128.43 (d), 129.90 (d), 130.42 (d), 132.50 (s), 132.51 (s), 132.75 (s), 133.22 (s), 133.68 (s), 134.80 (s), 134.90 (s), 135.80 (s), 138.60 (s); HRMS Calcd for $C_{27}H_{18}S_3$: 438.057, found 438.056; Anal. Calcd for $C_{27}H_{18}S_3$: C, 73.94; H, 4.14; S, 21.93. Found C, 73.81; H, 4.17; S, 21.93.

**2-Methyl-9-(9'H-thioxanthene-9'-ylidene)-9H-thioxanthene (1)**
To a stirred solution of **12** (438 mg, 1.00 mmol) in p-xylene (30 mL) was added copper powder (0.64 g, 10.0 mmol). After refluxing for 2 h the mixture was cooled to room temperature. The brown coloured copper salts were removed by filtration, the residue washed with $CH_2Cl_2$ (20 mL) and the solvents removed in vacuo. A yellow wet solid was obtained, which yielded after crystallization from absolute ethanol (≈ 400 mL) **1** as a white crystalline solid (372 mg, 0.92 mmol, 91.6%): mp 248.3-249.5 °C; $^1$H NMR (300 MHz) $\delta$ 2.00 (s, 3H), 6.58 (d, $J$ = 1.0 Hz, 1H), 6.81-6.95 (m, 7H), 7.09-7.14 (m, 3H), 7.41 (d, $J$ = 7.9 Hz, 1H), 7.51-7.55 (m, 3H); $^{13}$C NMR $\delta$ 20.75 (q), 125.30 (d), 125.41 (d), 125.55 (d), 126.46 (d), 126.57 (d), 126.78 (d), 126.88 (d), 126.89 (d), 127.42 (d), 127.43 (d), 127.44 (d), 129.66 (d), 129.67 (d), 129.68 (d), 130.26 (d), 131.94 (s), 133.46 (s), 133.47 (s), 135.26 (s), 135.27 (s), 135.36 (s), 135.53 (s), 135.67 (s), 135.76 (s), 135.86 (s), 135.94 (s); HRMS calcd for $C_{27}H_{18}S_2$: 406.085, found 406.085; Anal. calcd for $C_{27}H_{18}S_2$: C, 79.77; H, 4.46; S, 15.77. Found: C, 80.01; H, 4.41; S,

15.74.

***Cis* and *trans* dispiro[2-methoxy-9H-thioxanthene-9, 2'-thiirane-3', 9"-(2"-methyl)-9"H-thioxanthene] (13, 14)**

These compounds were prepared following the procedure described for **11**. Starting from hydrazone **8** (0.72 g, 3.00 mmol) and thioketone **11** (542 mg, 2.10 mmol), episulfides **13** and **14** were obtained as slightly pink powders (698 mg, 1.49 mmol, 71.1%, based upon the amount of added thioketone): $^1$H NMR (300 MHz, no clear distinction could be made between the NMR data of the cis isomer **13** and trans isomer **14**) $\delta$ 2.24 (s, 3H, $CH_3$), 2.28 (s, 3H, $CH_3$), 3.79 (s, 3H, $OCH_3$), 3.81 (s, 3H, $OCH_3$), 6.54-6.60 (m, 2H), 6.77-7.20 (m, 18H), 7.33-7.36 (m, 2H), 7.50 (s, 1H), 7.58 (s, 1H), 7.68-7.79 (m, 4H); $^{13}$C NMR $\delta$ (only the data for one isomer are given) 20.93 (q), 55.48 (q), 66.50 (s, C-S), 66.51 (s, C-S), 113.42 (d), 116.21 (d), 124.56 (d), 125.03 (d), 125.60 (d), 125.76 (d), 126.68 (d), 126.78 (d), 127.44 (d), 127.57 (d), 130.46 (d), 130.55 (d), 130.62 (d), 130.71 (d), 131.13 (s), 131.41 (s), 131.92 (s), 133.06 (s), 133.19 (s), 134.55 (s), 134.71 (s), 135.89 (s), 136.04 (s), 157.56 (s); HRMS Calcd for $C_{28}H_{20}S_3O$: 468.068, found 468.067

***Cis* and *trans* 2-methoxy-9-(2'-methyl-9'H-thioxanthene-9'-ylidene)-9H-thioxanthene (4, 5)**

These compounds were prepared following the procedure described for **1**. Starting from episulfides **13** and **14** (468 mg, 1.00 mmol), crystallization from ethanol (± 300 mL) furnished alkenes **4** and **5** as slightly yellow solids (357 mg, 0.82 mmol, 82.1%) as a cis/trans mixture (ratio **4:5**, 50:50): $^1$H NMR (300 MHz, no clear distinction could be made between the NMR data of the cis isomer **4** and trans isomer **5**) $\delta$ 2.01 (s, 3H, $CH_3$), 2.06 (s, 3H, $CH_3$), 3.34 (s, 3H, $OCH_3$), 3.35 (s, 3H, $OCH_3$), 6.31-6.34 (m, 2H), 6.59 (s, 1H), 6.67 (s, 1H), 6.70-7.44 (m, 20H), 7.53 (d, $J$ = 7.8 Hz, 4H); $^{13}$C NMR $\delta$ (only the data for one isomer are given) 20.88 (q), 55.07 (q), 113.88 (d), 114.97 (d), 125.35 (d), 125.60 (d), 125.70 (d), 126.65 (d), 126.71 (d), 127.03 (d), 127.60 (d), 127.67 (d), 127.85 (d), 127.94 (d), 129.84 (d), 129.86 (d), 131.95 (s), 132.17 (s), 133.49 (s), 133.60 (s), 135.56 (s), 135.57 (s), 135.66 (s), 135.67 (s), 135.83 (s), 136.04 (s), 136.97 (s), 157.85 (s); HRMS Calcd for $C_{28}H_{20}S_2O$: 436.096, found 436.096.

***Cis* and *trans* 2-methyl-9-(2'-methyl-9'H-thioxanthene-9'-ylidene)-9H-thioxanthene (2, 3)**

A solution of 2-methyl-thioxanthene-9-one (**15**, 2.26 g, 10.0 mmol) in oxalyl chloride (10 mL) was stirred and refluxed for 2 h. The brown solution was cooled to 20 °C and the excess oxalyl chloride removed under reduced pressure. The yellow brown residue was stripped with toluene (1 x 50 mL) to remove traces of oxalyl chloride and then dissolved in p-xylene (30 mL). Cu powder (4.0 g, 62.9 mmol) was added and the dark brown mixture stirred and refluxed for 5 h. After cooling and filtration the solvent was removed under reduced pressure to afford a brown solid (2.0 g). This brown solid was stirred with ethanol (100 mL) to remove some starting material. The residue (1.80 g) was crystallized from ethanol (approximately 500 mL) to yield **2** and **3** (1.43 g, 3.41 mmol, 68.2%) as a cis/trans mixture (ratio **2:3**, 58:42): $^1$H NMR (300 MHz) $\delta$ 2.04 (s, 6H, *cis*-$CH_3$), 2.05 (s, 6H, *trans*-$CH_3$), 6.63 (s, 4H), 6.82-7.20 (m, 16H), 7.45 (d, $J$ = 8.0 Hz, 4H), 7.57 (d, $J$ = 7.6 Hz, 4H); $^{13}$C NMR $\delta$ (in the aromatic region only the data for the cis isomer were fully resolved) 20.82 (q, *trans*-$CH_3$), 20.91 (q, *cis*-$CH_3$); cis isomer: 125.39 (d), 126.61 (d), 126.73 (d), 126.94 (d), 127.61 (d), 129.87 (d), 130.49 (d), 132.02 (s), 133.41 (s), 135.47 (s), 135.71 (s), 135.83 (s), 135.98 (s); HRMS Calcd for $C_{28}H_{20}S_2$: 420.101, found 420.100; Anal. Calcd for $C_{28}H_{20}S_2$: C, 79.96; H, 4.79; S, 15.25. Found. C, 79.12; H, 4.76; S, 15.11.

***Cis* and *trans* 2-methoxy-9-(2'-methoxy-9'H-thioxanthene-9'-ylidene)-9H-thioxanthene (6, 7)**

These compounds were prepared following the procedure described for **2** and **3**. Starting from 2-methoxy-9H-thioxanthene-9-one (**16**, 860 mg, 3.55 mmol), alkenes **6** and **7** were obtained as slightly yellow solids (560 mg, 1.24 mmol, 69.8 %) as a cis/trans mixture (ratio **6:7**, 38:62 after crystallization from ethanol (± 300 mL)): $^1$H NMR (300 MHz) $\delta$ 3.33 (s, 6H, *trans*-$OCH_3$), 3.38 (s, 6H, *cis*-$OCH_3$),

6.31 (d, $J$ = 2.6 Hz, 2H), 6.38 (d, $J$ = 2.6 Hz, 2H), 6.71 (dd, $J$ = 8.6, 2.8 Hz, 2H, *trans*), 6.72 (dd, $J$ = 8.6, 3.5 Hz, 2H, *cis*), 6.69-6.97 (m, 8H), 7.12 (ddd, 4H), 7.39 (d, $J$ = 8.8 Hz, 2H), 7.40 (d, $J$ = 8.8 Hz, 2H), 7.52 (dd, $J$ = 7.7, 1.1 Hz, 4H); $^{13}$C NMR $\delta$ 54.98 (q), 55.12 (q), 113.74 (d), 113.95 (d), 114.90 (d), 125.56 (d), 126.51 (s), 126.59 (d), 126.63 (d), 126.72 (s), 126.91 (d), 126.96 (d), 127.81 (d), 127.85 (d), 129.65 (d), 129.86 (d), 133.58 (s), 135.55 (s), 135.65 (s), 135.92 (s), 136.09 (s), 136.87 (s), 136.96 (s), 157.79 (s), 157.89 (s); HRMS Calcd for $C_{28}H_{20}S_2O_2$: 452.090, found 452.089.

**Crystal structure determination of 17**

The crystal structure determination of **17** was performed on a white crystal of approximate dimensions 0.30 x 0.20 x 0.20 mm obtained by crystallization from absolute ethanol. *Crystal data*: $C_{27}H_{18}OS$, $M_r$ = 390.51, monoclinic, $P2_1/n$, a = 12.246(1), b = 9.393(4), c = 17.610(2) Å, $\beta$ = 99.04°(1), $V$ = 2000.5 Å$^3$, Z = 4, $D_x$ = 1.297 gcm$^{-3}$, $\lambda$(MoK$\alpha$) = 0.70930 Å, $\mu$ = 1.684 cm$^{-1}$, F(000) =816, T = 293 K, $R_f$ = 0.069 for 1700 unique observed reflections with I $\geq$ 3.0 $\sigma$(I) and 262 parameters.

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