Bis[oxo/thioxothiazolinyl] Aromatic Compounds – Synthesis and Conformational Assignment

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Keywords: Atropisomerism / Conformational assignment / Chiral liquid chromatography / Diastereomer separation

A series of bis(oxo/thioxothiazolinyl) aromatic atropisomers with two chiral C(aryl)–N(heterocycle) axes was synthesized. The separation of *antiparallel*, *parallel* diastereomers was achieved by chromatography on silica. Conformational assignment for the bis-thione atropisomers **1a,b**–**4a,b** and bis-one atropisomers **9a,b**–**12a,b** was based on polarimetric results in analytical chiral chromatography on microcrystalline cellulose triacetate. The relationship conformation–^{1}H NMR chemical shifts, found for the bis-thiones and bis-ones was successfully applied for the conformational assignment of thione-one atropisomers not assigned by chiral liquid chromatography.

Introduction

Bis(thioxothiazolinyl) compounds having two thioxothiazoline heterocyclic units linked by alkylene, arylene, or arene groups are useful in photographic arts. Such compounds were described by Katritzky in a patent,[1] although their synthesis, characterization, and stereochemistry were not discussed.

The synthesis of the bis(thioxothiazolinyl) aromatic compounds by the bis(dithiocarbamate salt) route seemed challenging, since it was reported by Katritzky that "attempts to prepare and isolate bis(dithiocarbamate salts) from aromatic diamines were unsuccessful and gave instead the monodithiocarbamate salts".[2]

In this paper, we report the first documented synthesis of a series of bis(thioxothiazolinyl) aromatic compounds and their oxygenated congeners with general formula **A** (Scheme 1), as well as the separation and assignment of their conformational isomers.

The bis(oxo/thioxothiazolinyl) aromatic compounds are stereochemically interesting. While a large amount of information is available for nonheterocyclic, [3–13] and even for heterocyclic [14–17] atropisomers with two or more stereogenic C–C axes there are not many examples of atropisomers with two C(aryl)–N(heterocycle) stereogenic axes. Atropisomerically chiral systems with two chiral axes containing both aryls and heterocycles, namely 1,8 di-hetarylnaphthalenes[16,17] were recently investigated as model compounds for understanding the nature of electrostatic interactions involved during molecular recognition in systems such as proteins, nucleic acids, and host-guest pairs.

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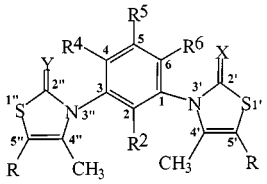
Compounds

Numbering of the compounds **A** is presented in Scheme 1 according to the nature of heteroatoms X and Y, and the nature of substituents R^2 – R^6 on the aromatic ring. Since $R^4 = R^6$, the positions ' and '' in the heterocycles are equivalent except for those in compounds **5a,b**–**8a,b** which are rendered nonequivalent by X ≠ Y. In compounds **a** R = H and in compounds **b** R = Me in 5', 5'' positions of the heterocycles.



A
a: R = H; **b:** R = CH_3

	X = Y = S	X = S; Y = O	X = Y = O
$R^2 = CH_3$; $R^4 = R^5 = R^6 = H$	**1**	**5**	**9**
$R^2 = H$; $R^4 = R^5 = R^6 = CH_3$	**2**	**6**	**10**
$R^2 = CH_3$; $R^4 = R^5 = R^6 = CH_3$	**3**	**7**	**11**
$R^2 = CH_3$; $R^4 = R^6 = H$; $R^5 = CH(CH_3)_2$	**4**	**8**	**12**

Scheme 1. Bis(oxo/thioxothiazolinyl) aromatic compounds **1a,b**–**12a,b**

The systematic names of the compounds are given in the Experimental Section. For convenience, the following abbreviations will be used: the compounds **1a,b**–**4a,b** (X = Y = S) will be named bis-thiones, compounds **5a,b**–**8a,b** (X = S, Y = O) thione-ones, and compounds **9a,b**–**12a,b** (X = Y = O) bis-ones.

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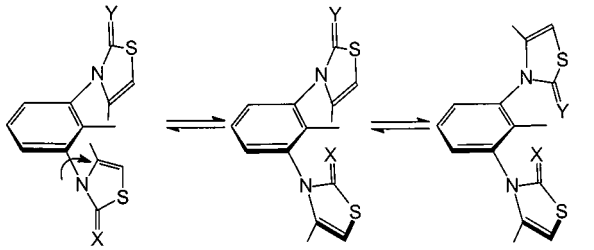
Stereochemistry

Steric hindrance around the C(aryl)–N(heterocycle) bonds in compounds **A** renders the two heterocycles nonplanar to the central aromatic ring giving rise to racemic (C_2 symmetry) and *meso* (plane of symmetry) conformational diastereomers as in the case of 1,8-dipyridylnaphthalenes.[17]

Two relative positions of C=X and C=Y groups are possible: on the same side (*parallel* conformation) and on opposite sides (*antiparallel* conformation) of the central aromatic ring. For the bis-thiones **1a,b**–**4a,b** and bis-ones **9a,b**–**12a,b** the *antiparallel* conformation corresponds to a racemic (C_2 symmetry) while the *parallel* conformers are *meso* (σ plane). For the thione-ones **5a,b**–**8a,b** both *parallel* and *antiparallel* conformers are chiral being devoid of any element of symmetry.

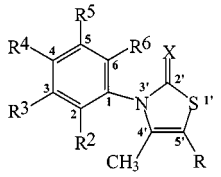


Scheme 2. Stereochemistry and interconversion of bis(oxo/thioxothiazolinyl) aromatic compounds

The *parallel*/*antiparallel* interconversion occurs principially by a single 180° rotation of one heterocycle around the C(aryl)–N(heterocycle) bond. Racemization occurs by sequential rotation of both heterocycles (Scheme 2).

Hindered rotation about the C(aryl)–N(heterocycle) bond in the corresponding compounds **B**, with only one chiral axis (Scheme 3), was extensively studied by some of the present authors. For similar substitution in positions 2 and 6, the dynamics of the rotation in compounds **A** and **B** should be the same. For compounds **B** having R^2 = Me and $R^3 = R^4 = R^5 = R^6$ = H the values of the rotational barrier $\Delta G^{\neq}$ were found to be 122 kJ/mol (polarimetric experiment) when X = O, and greater than 134 kJ/mol at 360.15 K when X = S.[18,19]

Since all the compounds **A** in Scheme 1 are substituted in positions 2/6 with Me/H or Me/Me, $\Delta G^{\neq}$ values of the same magnitude or higher are expected. This signifies that compounds **A** should be conformationally stable, no rotation around the C(aryl)–N(heterocycle) bond being expected to occur at room temperature. However, conformational interconversion may occur for thione-ones and bis-ones at higher temperatures by the rotation of one oxothiazoline ring.



B
a: R = H; **b**: R = CH_3

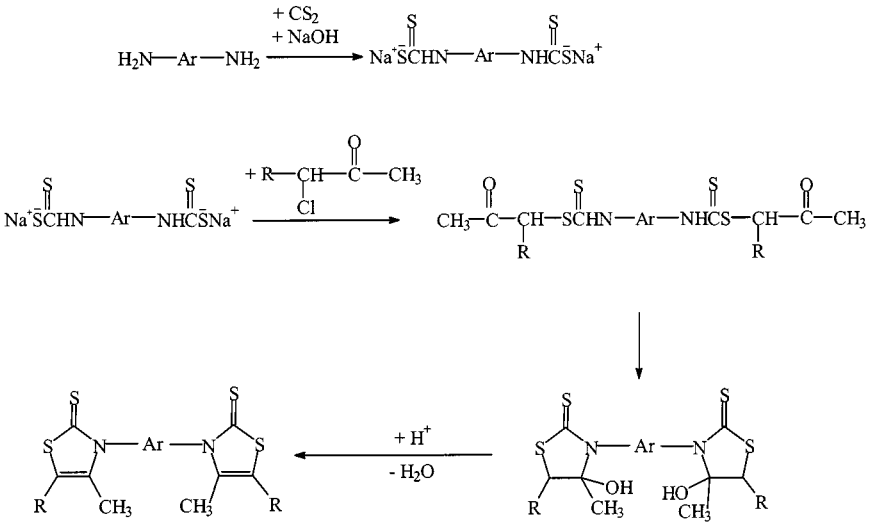
	X = S	X = O
$R^2 = CH_3$; $R^3 = R^4 = R^5 = R^6 = H$	**13**	**15**
$R^2 = R^3 = H$; $R^4 = R^5 = R^6 = CH_3$	**14**	**16**

Scheme 3. Mono(oxo/thioxothiazolinyl) aromatic compounds **13a,b**–**16 a,b**

Results and Discussion

Synthesis

The bis-thiones **1a,b**–**4a,b** were synthesized according to Scheme 4. Starting from aromatic diamines, reaction with sodium hydroxide and carbon disulfide yielded the corres-



Scheme 4. Synthesis of bis-thiones **1a,b**–**4a,b**

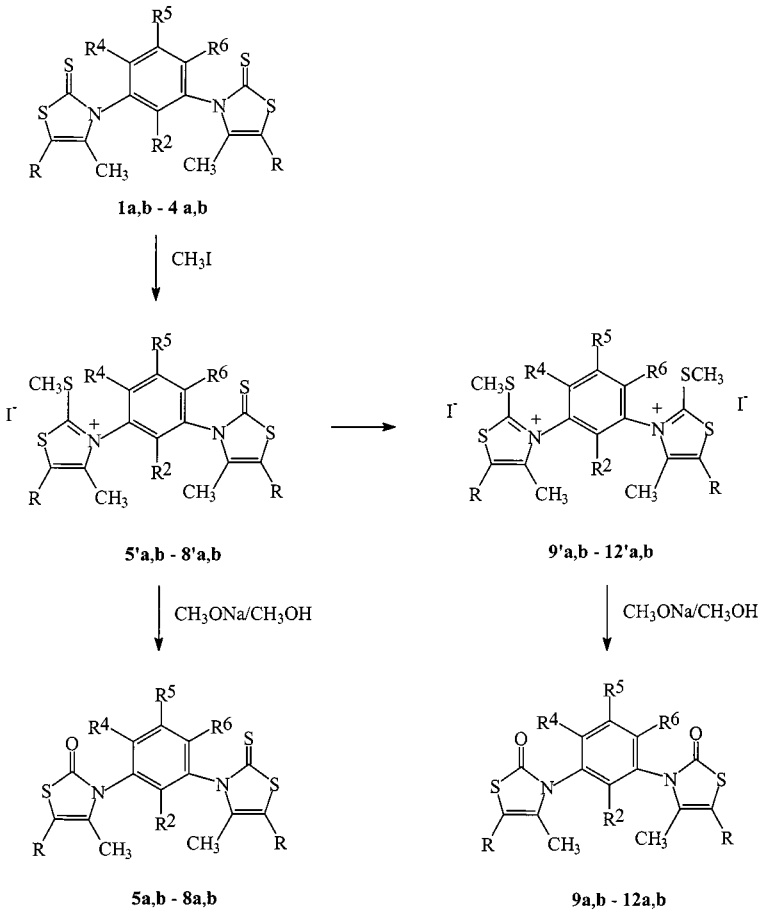
ponding bis(dithiocarbamates). The bis(dithiocarbamate) was not isolated but was further reacted with the corresponding α-chloro ketone (1-chloropropane-2-one for compounds **a** and 3-chlorobutane-2-one for compounds **b**), and the isolated product was dehydrated in acidic medium to yield the bis-thione. The synthesis of the aromatic bis(dithiocarbamate) is an adaptation of Garin's method,[20] while the formation of the heterocycles is an adaptation of the method described by Katritzky for bis-thiones.[1]

The synthesis resulted in the mixture of the two diastereomeric forms, *antiparallel* and *parallel*, in unequal amounts according to the ^{1}H-NMR spectrum of the crude reaction product. The diastereomers were separated by chromatography on silica gel (eluent chloroform/ethyl acetate 9:1) and were independently characterized by m.p., UV, ^{1}H- and ^{13}C-NMR data. Unambiguous conformational assignment was achieved by chiral liquid chromatography on microcrystalline cellulose triacetate (vide infra).

The thione-ones **5a,b**–**8a,b** and the bis-ones **9a,b**–**12a,b** were synthesized from the corresponding bis-thiones **1a,b**–**4a,b** by the series of reactions presented in Scheme 5.

The method is an adaptation of the procedure used by Kashima and Katoh for preparing 1-arylpyrimidin-2-ones from 1-arylpyrimidine-2-thiones,[21] which has been successfully applied for converting C=S into C=O in the series **B**.[18] The transformation occurs via the intermediate mono-thiazolinium salts **5'a,b**–**8'a,b** and bis-thiazolinium salts **9'a,b**–**12'a,b**. The solubility of these salts in the reaction mixture had a drastic effect on the reaction course. Compounds **1a** and **3a** yielded the crystallized mono-thiazolium salts **5'a** and **7'a**, respectively, which ultimately yielded the pure thione-ones **5a** and **7a**, respectively. Compounds **2a,b**, **3b**, and **4a,b** yielded the crystallized bis-thiazolium salts **10'a,b**, **11'b** and **12'a,b** respectively, and ultimately yielded the pure bis-ones **10a,b**, **11b** and **12a,b**. For the other compounds, neither the mono- nor the bis-thiazolinium salt crystallized; the reaction product was actually a mixture of the two oxygenated compounds (the thione-one and the bis-one) together with some traces of the starting bis-thione.

The conversion of the thioxothiazolinyl ring to the oxothiazolinyl ring via the thiazolinium salt is known to occur with conservation of stereochemistry. No racemization was observed[18] in preparing *N*-arylthiazolinones **15a** and **b** from the optically active *N*-arylthiazolinethiones **13a** and **b**. The same holds true for the reactions in Scheme 5, since starting from a single diastereomer of bis-thione only one diastereomer of thione-one and/or bis-one was obtained. When the reaction was performed with mixtures of diastereoisomers, the oxygenated compounds were obtained as a



Scheme 5. Synthesis of thione-ones **5a,b**–**8a,b** and of bis-ones **9a,b**–**12a,b**

mixture of diastereomers in the same ratio as in the starting compound.

Both the diastereomers of bis-ones and of thione-ones could be separated by chromatography on silica gel (eluent: chloroform/ethyl acetate, 9:1).

Conformational Assignment by Chiral Liquid Chromatography

Chiral chromatography is a very convenient way to ascertain *meso* versus D,L relationship for diastereomers in general.[22–25] There are two methods currently used in the literature. The first one consists of comparing the nonchiral chromatogram with the chiral one. One of the two peaks in the achiral chromatogram, which corresponds to the chiral diastereomer, will be split under chiral conditions. The second method uses only chiral chromatography with both UV and polarimetric or CD detection. For the conformational assignment of *parallel*/*antiparallel* pairs of bis-thiones and *parallel*/*antiparallel* pairs of bis-ones, for which the *parallel* conformer is achiral while the *antiparallel* conformer is racemic, we used the chiral liquid chromatography on microcrystalline cellulose triacetate (CTA, eluent ethanol 96%) with both UV and polarimetric detection.

For the bis-thiones **1a,b**–**4a,b** each diastereomer (separated as previously shown by chromatography on silica gel) was in turn subjected to chiral chromatography. This allowed unambiguous conformational assignment based on the polarimetric response: the *antiparallel* conformers showed two absorption maxima (a positive and a negative one), while for the *parallel* conformers the polarimetric line showed no deviation from zero (*meso*).

For the bis-ones **9a,b**, **10a**, **11a,b**, and **12b**, each diastereomer (previously separated by chromatography on silica gel) was subjected to chiral chromatography on microcrystalline cellulose triacetate in order to assign conformation using the same principle.

Table 1 presents the polarimetric response in chiral liquid chromatography on microcrystalline cellulose triacetate (CTA) for the bis-thiones **1a,b**–**4a,b** with the order of signs indicating the actual elution order of the enantiomers, together with the R_f values (TLC on silica gel) of the *parallel*/*antiparallel* conformers, the melting points of each conformer, and the conformational composition of the crude crystallized product determined from the ^{1}H-NMR spectrum.

Examination of the data in Table 1 shows the prevalence of the chiral *antiparallel* conformer in the reaction mixture. Another interesting observation is that the difference between the R_f values of the conformers ($\Delta R_f = R_f^{antiparallel} - R_f^{parallel} \approx 0.3$) is almost constant within the series, with the *antiparallel* conformer having the higher R_f. This could be explained if one considers that the interaction with the support is mainly dipolar in nature. The *parallel* conformer with two adjacent polar C=S groups is prone to stronger interaction than the *antiparallel* conformer having these polar groups on opposite sides of the molecule.

Interestingly the total dipoles of the two diastereomers of bis-thiones calculated by AM1 or PM3 optimized structures with TSAR software[26] are drastically different both in size and direction. Values for the *antiparallel* form are in the range 0.8–1.6 D, depending on the compound and the method of calculation, the dipole direction being into the plane of the aryl ring along the C-2, C-5 carbon atoms. Dipole values for the *parallel* form are in the range 8–10 D and the dipole direction is perpendicular to the aryl ring.

Bis-ones **9a,b**–**12a,b** were also fully characterized (see Experimental Section) and as for the bis-thiones, the same relationship R_f antiparallel $> R_f$ parallel is respected.

Table 1. Characterization of the bis(thioxothiazoline) aromatic compounds **1a,b**–**4a,b**

Compound	Conf.	Molar fraction[a]	m.p., °C[b]	R_f[c]	Polarimetric response[d]
1a	*antiparallel*	0.65	282–283	0.58	–/+
	parallel	0.35	320–322	0.24	0
1b	*antiparallel*	0.64	271–272	0.65	+/–
	parallel	0.36	> 320	0.35	0
2a	*antiparallel*	1	287–288	0.60	+/–
	parallel	0	272–274	0.25[e]	0
2b	*antiparallel*	0.75	294	0.78	+/–
	parallel	0.25	288–290	0.42	0
3a	*antiparallel*	0.66	314	0.66	+/–
	parallel	0.33	> 340	0.37	0
3b	*antiparallel*	0.73	266–270	0.74	+/–
	parallel	0.27	> 320	0.48	0
4a	*antiparallel*	0.88	240–244	0.63	–/+
	parallel	0.12	220–224	0.39	0
4b	*antiparallel*	1	204–206	0.80	–/+
	parallel	0	–	0.39[e]	0

[a] Determined by integration from the ^{1}H-NMR spectrum (300 MHz) of the crude crystallized product. – [b] Values for the racemic *antiparallel* conformer and *meso parallel* conformer. – [c] Thin-layer chromatography on silica gel, eluent $CHCl_3$/AcOEt, 9:1. – [d] 0 signifies no deviation from zero of the polarimetric line; +/– signifies two maxima (positive and negative) of the polarimetric line; the order of signs corresponds to the elution order of enantiomers. – [e] Minor isomer isolated by work-up of the mother liquor.

Relationship between Conformation and NMR Chemical Shifts

Due to the symmetry properties and the substitution pattern in the bis-thiones **1a,b**–**4a,b** as well as in the bis-ones **9a,b**–**12a,b**, the methyl groups in the 4' and 4" positions are equivalent in *antiparallel* conformers and enantiotopic in the *parallel* conformers. Accordingly, the 4'- and 4''-methyl groups are expected to be isochronous.

Examination of the ^{1}H-NMR data of unambiguously assigned *parallel*/*antiparallel* conformers of bis-thiones **1a,b**–**4a,b** and bis-ones **9a,b**–**12a,b** revealed the fact that for each compound the signal of the 4',4"-Me_2 groups is always upfield in the *parallel* conformer compared to the *antiparallel* conformer.

The signal is a doublet in bis-thiones **1a**–**4a** and bis-ones **9a**–**12a** due to the cisoid allylic coupling with the 5'-H (5"-H) (J_{thione} = 1.1 Hz and J_{one} = 1.2 Hz) and a quadruplet in bis-thiones **1b**–**4b** and bis-ones **9b**–**12b** due to the cisoid homoallylic coupling to 5'-Me (5''-Me) (J_{thione} = 0.8 Hz and J_{one} = 0.7 Hz. This multiplicity avoided any confusion in assignments with the other methyl groups on the central aromatic ring.

It should also be noted that the difference between the chemical shifts of 4',4''-Me groups in the *antiparallel* conformer and the *parallel* conformer is almost a constant within both the series of bis-thiones ($\Delta\delta_{thione} = \delta_{thione}^{antiparallel} - \delta_{thione}^{parallel} = 0.09 \pm 0.01$ ppm) and bis-ones ($\Delta\delta_{one} = \delta_{one}^{antiparallel} - \delta_{one}^{parallel}$ = 0.05–0.08 ppm) being large enough to allow the determination by integration of the conformational composition in mixtures of conformers.

On the other hand, the *parallel* conformers of the bis-thiones **1a,b** and **2a,b** and their respective mono(thioxothiazolinyl) aromatic compounds **13a,b** and **14 a,b**, as well as the *parallel* conformers of the bis-ones **9a,b** and **10a,b** and the mono(oxothiazolinyl) aromatic compounds **15a,b** and **16a,b**, respectively, with the same substituent pattern have almost the same δ values for the 4',4''-Me_2 groups and for the 4'-Me group, respectively (see Table 2).

Table 2. Chemical shifts of 4',4''-Me_2 protons in bis- and related mono(oxo/thioxothiazolinyl) aromatic compounds ($CDCl_3$, 300 MHz)

Compound	Conf.	$\delta_{4'\text{-Me}}$	Compound[Ref.]	$\delta_{4'\text{-Me}}$
1a	*antiparallel*	1.98		
	parallel	1.88	**13a**[12]	1.89
1b	*antiparallel*	1.87		
	parallel	1.77	**13b**[12]	1.78
2a	*antiparallel*	1.97		
	parallel	1.89	**14a**[6]	1.87
2b	*antiparallel*	1.86		
	parallel	1.77	**14b**[6]	1.77
9a	*antiparallel*	1.85		
	parallel	1.77	**15a**[2]	1.74
9b	*antiparallel*	1.75		
	parallel	1.67	**15b**[2]	1.67
10a	*antiparallel*	1.85		
	parallel	1.80	**16a**[6]	1.79
10b	*antiparallel*	1.74		
	parallel	1.69	**16b**[6]	1.72

This means that replacement of R^3 in compounds **B** (X = O or S) with a second heterocycle (identical with the existent one) in *parallel* relative position had only a small or no influence on the chemical shift of the 4'-Me group, whereas the same operation but in the *antiparallel* relative position lead to a definite downfield shift of this signal. In each diastereomeric pair of bis-ones or bis-thiones, the chemical shift difference ($\Delta\delta = \delta_{4',4''\text{–Me2}}^{antiparallel} - \delta_{4',4''\text{–Me2}}^{parallel}$) is actually the measure of the through-space deshielding effect of the exocyclic heteroatom on the 4''(4')-methyl group located on the same side of the central ring in the second heterocycle.

This "*trans* conformational shift" effect Δδ was in the range of 0.08–0.10 ppm for X = S and of 0.05–0.08 ppm for X = O and was used in the conformational assignment of the thione-ones **5a,b**–**8a,b**.

Conformational Assignment for the (Thioxothiazolinyl) (Oxothiazolinyl) Aromatic Compounds

As was already mentioned, the *parallel* and *antiparallel* conformers of thione-ones **5a,b**–**8a,b** are both chiral. Therefore, chiral chromatography can no longer discriminate between conformers, since both may be resolved in enantiomers. In this case, conformation was assigned using the previously independently established relationships: conformation – R_f values in TLC and conformation – ^{1}H-NMR δ values of the 4'-Me, 4''-Me probe groups, according to the data displayed in Table 3.

The diastereomers of thione-ones were arranged according to the order of R_f values, namely in each pair the isomer with higher R_f was assigned the *antiparallel* conformation. This assignment was checked by comparing the experimental δ values for the 4'-Me, 4''-Me groups in thione-ones with values calculated according to the correlation between conformation and ^{1}H-NMR chemical shifts presented above. The data used for calculation were:

– the chemical shifts of 4',4''-Me_2 groups in *parallel* bis-thiones $(\delta_{4',4''\text{–Me2}})_{bis\text{-}thione}^{parallel}$ and *parallel* bis-ones $(\delta_{4',4''\text{–Me2}})_{bis\text{-}one}^{parallel}$

– the "*trans* conformational shift" due to the (thio)carbonyl group, namely:

$$(\Delta\delta)_{C=S} = (\delta_{4',4''\text{–Me2}})_{bis\text{-}thione}^{antiparallel} - (\delta_{4',4''\text{–Me2}})_{bis\text{-}thione}^{parallel} \quad (1)$$

$$(\Delta\delta)_{C=O} = (\delta_{4',4''\text{–Me2}})_{bis\text{-}one}^{antiparallel} - (\delta_{4',4''\text{–Me2}})_{bis\text{-}one}^{parallel} \quad (2)$$

The chemical shifts for the 4'-CH_3 and 4''-CH_3 groups in thione-ones (which are no longer equivalent, since X ≠ Y) were calculated as follows:

– in the *parallel* conformer

$$(\delta_{4'\text{–Me}})_{thione\text{-}one}^{parallel} = (\delta_{4',4''\text{–Me2}})_{bis\text{-}thione}^{parallel} \quad (3)$$

and

$$(\delta_{4''\text{–Me}})_{thione\text{-}one}^{parallel} = (\delta_{4',4''\text{–Me2}})_{bis\text{-}one}^{parallel} \quad (4)$$

as it was shown that the second heterocycle had no influence on the chemical shift of the 4'-Me (or 4''-Me) when in parallel conformation;

Table 3. R_f values and ^{1}H NMR chemical shifts of the 4'-Me and 4''-Me in bis-thiones **1a**,**b**–**4a**,**b**, bis-ones **9a**,**b**–**12a**,**b**, and thione-ones **5a**,**b**–**8a**,**b** [δ values in brackets calculated by Equations (1)–(6)]

Compd.	Conf.	R_f[a]	$\delta_{4'\text{-Me}}$	$\delta_{4''\text{-Me}}$	Compd.	Conf.	R_f[a]	$\delta_{4'\text{-Me}}$	$\delta_{4''\text{-Me}}$
1a[b]	*antiparallel*	0.58	1.98	1.98	**3a**[b]	*antiparallel*	0.66	1.91	1.91
	parallel	0.24	1.88	1.88		*parallel*	0.37	1.82	1.82
9a[b]	*antiparallel*	0.35	1.85	1.85	**11a**[b]	*antiparallel*	0.49	1.77	1.77
	parallel	0.08	1.77	1.77		*parallel*	0.15	1.70	1.70
5a	*antiparallel*	0.37	1.97	1.87	**7a**	*antiparallel*	0.44	1.91	1.78
			(1.96)	(1.87)				(1.89)	(1.79)
	parallel	0.17	1.86	1.79		*parallel*	0.21	*	*
			(1.88)	(1.77)				(1.82)	(1.70)
1b[b]	*antiparallel*	0.65	1.87	1.87	**3b**[b]	*antiparallel*	0.74	1.82	1.82
	parallel	0.35	1.77	1.77		*parallel*	0.48	1.72	1.72
9b[b]	*antiparallel*	0.34	1.75	1.75	**11b**[b]	*antiparallel*	0.5	1.68	1.68
	parallel	–	1.67	1.67		*parallel*	0.1	1.61	1.61
5b	*antiparallel*	0.35	1.86	1.76	**7b**	*antiparallel*	0.52	1.81	1.69
			(1.85)	(1.77)				(1.79)	(1.71)
	parallel	0.12	1.76	1.69		*parallel*	–	*	*
			(1.77)	(1.67)				(1.72)	(1.61)
2a[b]	*antiparallel*	0.60	1.97	1.97	**4a**[b]	*antiparallel*	0.63	1.95	1.95
	parallel	0.25	1.89	1.89		*parallel*	0.39	1.87	1.87
10a[b]	*antiparallel*	0.3	1.85	1.85	**12a**	*antiparallel*	0.4	1.84	1.84
	parallel	0.2	1.80	1.80		*parallel*	0.11	*	*
6a	*antiparallel*	0.61	1.95	1.88	**8a**	*antiparallel*	0.47	1.96	1.83
			(1.94)	(1.88)					
	parallel	0.41	1.87	1.80		*parallel*	–	*	*
			(1.89)	(1.80)				(1.87)	
2b[b]	*antiparallel*	0.78	1.86	1.86	**4b**[b]	*antiparallel*	0.80	1.86	1.86
	parallel	0.42	1.77	1.77		*parallel*	0.39	1.76	1.76
10b[b]	*antiparallel*	0.53	1.74	1.74	**12b**[b]	*antiparallel*	0.54	1.74	1.74
	parallel	0.12	1.69	1.69		*parallel*	–	1.66	1.66
6b	*antiparallel*	0.61	1.85	1.78	**8b**	*antiparallel*	0.6	1.86	1.74
			(1.82)	(1.78)				(1.84)	(1.76)
	parallel	0.27	1.77	1.71		*parallel*	–	*	*
			(1.77)	(1.69)				(1.76)	(1.66)

[a] TLC (silica gel, chloroform/ethyl acetate 9:1). – [b] Unambiguous conformational assignment by chiral liquid chromatography on CTA, eluent ethanol 96%.

− in the *antiparallel* conformer, the 4'-CH_3 and 4''-CH_3 chemical shifts were those from the *parallel* conformer plus the influence of the exocyclic heteroatom in the other heterocycle, namely C=O for 4'-CH_3 and C=S for 4''-CH_3:

$$(\delta_{4'\text{–Me}})^{\text{antiparallel}}_{\text{thione-one}} = (\delta_{4'\text{–Me}})^{\text{parallel}}_{\text{thione-one}} + (\Delta\delta)_{C=O} \quad (5)$$

$$(\delta_{4''\text{–Me}})^{\text{antiparallel}}_{\text{thione-one}} = (\delta_{4''\text{–Me}})^{\text{parallel}}_{\text{thione-one}} + (\Delta\delta)_{C=S} \quad (6)$$

A comparison, in Table 3, of the experimental ^{1}H-NMR chemical shifts with those calculated applying formulae (1)–(6) shows a good concordance for all thione-ones, therefore the two conformation assignment procedures gave the same result.

Conclusion

The series of bis(oxo/thioxothiazolinyl) aromatic atropisomers with two chiral C(aryl)–N(heterocycle) axes **1a,b**–**12a,b** was synthesized. The *antiparallel*/*parallel* diastereomers were separated by chromatography on silica. Conformational assignment was achieved by analytical chiral chromatography on microcrystalline cellulose triacetate with polarimetric detection for the bis-thione atropisomers **1a,b**–**4a,b** and bis-one atropisomers **9a,b-12a,b**, for which the *antiparallel* conformer is racemic, while the *parallel* conformer is a *meso* compound.

The two relationships conformation – R_f and conformation –^{1}H-NMR chemical shifts were found for the bis-thiones and bis-ones, and were independently applied for the conformational assignment of thione-one atropisomers not assigned by chiral liquid chromatography.

The series of bis(oxo/thioxothiazolinyl) aromatic atropisomers with two chiral C(aryl)–N(heterocycle) axes **1a,b**–**12a,b** may contribute, as model compounds, to studies on the chiral recognition mechanism in liquid chromatography on chiral stationary phases as an extension of the systematic studies already performed by some of the present authors on the corresponding atropisomers with only one chiral axis.[18,28–33]

Experimental Section

Liquid Chromatography on Microcrystalline Cellulose Triacetate: Cellulose triacetate (15–25 μm from Merck) packed in a thermostated 200 × 25 mm glass column equipped with a 5 cm^3 injection loop, UV (LKB 2138 UVICORD) and polarimetric (Perkin–Elmer 241) detectors were used. In all cases, the elution solvent was ethanol/water 96/4, flow rate 138 mL/h, pressure drop ca. 1.7 bar, temperature 25 °C. For analytical runs, 2–3 mg racemate were used; *k*'(–), *k*'(+) are given for the chiral conformer and *k*' for the achiral conformer, using 1,3,5-tri-*tert*-butylbenzene as a reference.

Apparatus: NMR spectra were recorded on a Varian Gemini 300 BB Spectrometer (^{1}H 300 MHz; ^{13}C 75.5 MHz) in $CDCl_3$. – Melt-

ing points are uncorrected and were measured on a Boetius apparatus. – UV spectra were obtained in methanol on a Beckman M-25 instrument. – The yields and the elemental analysis for the bisthiones **1a,b** – **4a,b** are given for the mixture of *parallel* and *antiparallel* conformers. The molar ratio of the two conformers in the crystallized product, the melting points and the R_f values for each of the two conformers were presented in Table 1. – For all compounds, assignment of the ^{1}H- and ^{13}C-NMR chemical shifts for each conformer was achieved from 1D (^{1}H, ^{13}C, APT) and 2D (HETCOR, COLOC) experiments.

General Procedure for the Synthesis of Bis(thioxothiazolinyl) Aromatic Compounds 1a,b–4a,b: The procedure was adapted from Katritzky's method (US Patent[1]) using a sodium bis(dithiocarbamate) prepared by a procedure adapted from J. Garin et al.[20] To a solution of aromatic bis-amine (1 mmol) in dry dimethyl sulfoxide (4 mL) maintained at 20 °C, under magnetic stirring, was added stepwise a 20 M aqueous sodium hydroxide solution (0.09 mL, 2 mmol) and carbon disulfide (0.12 mL, 2 mmol). The mixture was stirred for two hours at ambient temperature and then the α-chloro ketone (2 mmol) was added dropwise (1-chloropropan-2-one for compounds **a** and 3- chlorobutan-2-one for compounds **b**). After 45 min, the mixture was poured into cold water (25 mL). The precipitate which formed was filtered, and to the cake was added 10 mL ethanol (96%) and the solution acidified with hydrochloric acid 36% to pH = 1. The acidic solution was heated under reflux for three hours. The reaction was followed by TLC ($CHCl_3$/AcOEt, 9: 1) and UV spectroscopy (characteristic band for the thiazolinethione 320 nm, open chain 280 nm). Cooling to room temperature allowed the crystallization of the *antiparallel* and *parallel* conformers. Reported yields are given for the crystallized compound. All the compounds had a poor solubility in common solvents (ethanol, chloroform), however, for all the compounds a higher solubility of the *parallel* conformer in the reaction mixture (ethanol) was noticed.

2-Methyl-1,3-bis(4-methyl-2-thioxo-3-thiazolinyl)benzene (1a): Yield: 29%. – $C_{15}H_{14}N_2S_4$ (350): calcd. C 51.43, H 4.0, N 8.0, S 36.57; found C 51.85, H 4.69, N 8.02, S 36.36. – UV (MeOH): *antiparallel* λ_{max} = 323 nm (ε = 20000). – ^{1}H NMR ($CDCl_3$, 300 MHz) δ *antiparallel* = 1.80 (3 H, s), 1.98 (6 H, d, *J* = 1.1 Hz), 6.40 (2 H, q, *J* = 1.1 Hz), 7.33 (2 H, d, *J* = 7.9 Hz), 7.59 (1 H, t, *J* = 7.9 Hz); *parallel* = 1.86 (3 H, s), 1.88 (6 H, d, *J* = 1.2 Hz), 6.36 (2 H, q, *J* = 1.2 Hz), 7.35 (2 H, d, *J* = 8.0 Hz), 7.57 (1 H, t, *J* = 8.0 Hz). – ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ *antiparallel* = 12.56 (2-CH_3), 15.85 (4'-CH_3, 4''-CH_3), 106.67 (C5', C5''), 128.62 (C5), 129.82 (C4, C6), 135.99 (C1, C3), 138.70 (C2), 139.87 (C4', C4''), 189.39 (C2', C2''); *parallel* 13.07(2-CH_3), 15.77 (4'-CH_3, 4''-CH_3), 106.58 (C5', C5''), 128.51 (C5), 130.38 (C4, C6), 136.06 (C1, C3), 138.53 (C2), 138.83 (C4', C4''), 189.35 (C2', C2''). – CTA (EtOH 95%): *antiparallel k*'(+) = 1.39; *k*'(–) = 1.39; *parallel k*' = 0.94.

1,3-Bis(4,5-dimethyl-2-thioxo-3-thiazolinyl)-2-methylbenzene (1b): Yield: 30%. – $C_{17}H_{18}N_2S_4$ (378): calcd. C 53.97, H 4.76, N 7.41, S 33.86; found C 57.47, H 3.95, N 7.18, S 32.63. – UV (MeOH): *antiparallel* λ_{max} = 327 nm (ε = 16000); *parallel* λ_{max} = 322 nm (ε = 21000). – ^{1}H NMR ($CDCl_3$, 300 MHz) δ *antiparallel* = 1.81 ppm (3 H, s), 1.87 (6 H, q, *J* = 0.9 Hz), 2.22 (6 H, q, *J* = 0.9 Hz), 7.30 (2 H, d, *J* = 8.1 Hz), 7.55 (1 H, t, *J* = 8.1 Hz); *parallel* = 1.77 (6 H, q, *J* = 1.0 Hz), 1.87 (3 H, s), 2.20 (6 H, q, *J* = 1.0 Hz), 7.32 (2 H, d, *J* = 7.9 Hz), 7.53 (1 H, t, *J* = 7.9 Hz). – ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ *antiparallel* = 11.80 (5'-CH_3, 5''-CH_3), 12.63 (2-CH_3), 13.41 (4'-CH_3, 4''-CH_3), 118.32 (C5', C5''), 128.49 (C5), 129.59 (C4, C6), 134.65 (C1, C3), 135.85 (C2), 139.41 (C4', C4''), 187.08 (C2', C2''); *parallel* = 11.88 (5'-CH_3, 5''-CH_3), 12.69 (2-CH_3), 13.24 (4'-CH_3, 4''-CH_3), 118.12 (C5', C5''), 128.38 (C5), 130.18 (C4, C6), 133.28 (C1, C3), 135.68 (C2), 139.58 (C4', C4''), 187.28 (C2', C2''). – CTA (EtOH 95%): *antiparallel k*'(+) = *k*'(–) = 1.39; *parallel k*' = 0.94.

4,5,6-Trimethyl-1,3-bis(4-methyl-2-thioxo-3-thiazolinyl)benzene (2a): Yield: 45% – $C_{17}H_{18}N_2S_4$ (378): calcd. C 53.97, H 4.76, N 7.41, S 33.86; found C 54.20, H 4.65, N 7.60, S 33.99. – UV (MeOH): *antiparallel* λ_{max} = 316 nm (ε = 23000); *parallel* λ_{max} = 317 nm (ε = 23000). – ^{1}H NMR ($CDCl_3$, 300 MHz) δ *antiparallel* = 1.97 (6 H, d, *J* = 1.1 Hz), 2.05 (6 H, s), 2.36 (3 H, s), 6.36 (2 H, q, *J* = 1.1 Hz), 6.83 (1 H, s); *parallel* = 1.89 (6 H, d, *J* = 1.2 Hz), 2.08 (6 H, s), 2.37 (3 H, s), 6.32 (2 H, q, *J* = 1.2 Hz), 6.88 (1 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ *antiparallel* = 14.71 (4'-CH_3, 4''-CH_3), 15.81 (4-CH_3, 6-CH_3), 16.84 (5-CH_3), 106.25 (C5', C5''), 125.90 (C2), 135.39 (C4, C6), 136.38 (C1, C3), 139.63 (C5), 140.3 (C4', C4''), 189.42 (C2', C2''); *parallel* = 15.04 (4'-CH_3, 4''-CH_3), 15.94 (4-CH_3, 6-CH_3), 17.04 (5-CH_3), 106.21 (C5', C5''), 125.76 (C2), 135.52 (C4, C6), 136.95 (C1, C3), 138.94 (C5), 139.73 (C4', C4''), 189.63 (C2', C2''). – CTA (EtOH 95%): *antiparallel* k'(+) = 0.44; k'(–) = 0.86; *parallel* k' = 0.74.

1,3-Bis(4,5-dimethyl-2-thioxo-3-thiazolinyl)-4,5,6-trimethylbenzene (2b): Yield: 60% – $C_{19}H_{22}N_2S_4$ (406): calcd. C 56.16, H 5.42, N 6.90, S 31.53; found C 56.40, H 5.58, N 6.98, S 31.04. – UV (MeOH): *antiparallel* λ_{max} = 320 nm (ε = 35000); *parallel* λ_{max} = 318 nm (ε = 33000). – ^{1}H NMR ($CDCl_3$, 300 MHz) δ *antiparallel* = 1.86 (6 H, q, *J* = 0.8 Hz), 2.04 (6 H, s), 2.17 (6 H, q, *J* = 0.8 Hz), 2.34 (3 H, s), 6.80 (1 H, s); *parallel* = 1.77 (6 H, q, *J* = 0.9 Hz), 2.06 (6 H, s), 2.17 (6 H, q, *J* = 0.9 Hz), 2.34 (3 H, s), 6.85 (1 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ *antiparallel* = 11.61 (5'-CH_3, 5''-CH_3), 13.27 (4'-CH_3, 4''-CH_3), 14.67 (4-CH_3, 6-CH_3), 16.75 (5-CH_3), 117.74 (C5', C5''), 125.86 (C2), 135.04 (C4', C4''), 136.08 (C4, C6), 136.15 (C1, C3), 139.3 (C5), 187.08 (C2', C2''); *parallel* = 11.77 (5'-CH_3, 5''-CH_3), 13.30 (4'-CH_3, 4''-CH_3), 14.93 (4-CH_3, 6-CH_3), 16.87 (5-CH_3), 117.61 (C5', C5''), 125.54 (C2), 133.69 (C4', C4''), 136.23 (C4, C6), 136.55 (C1, C3), 139.31 (C5), 187.34 (C2', C2''). – CTA (EtOH 95%): *antiparallel k*'(+) = 0.22; *k*'(–) = 1.57; parallel *k*' = 0.16.

2,4,5,6-Tetramethyl-1,3-bis(4-methyl-2-thioxo-3-thiazolinyl)benzene (3a): Yield: 56% – $C_{18}H_{20}N_2S_4$ (392): calcd. C 55.10, H 5.10, N 7.14, S 32.65; found C 55.35, H 5.40, N 7.08, S 32.80. – UV (MeOH): *antiparallel* λ_{max} = 315 nm (ε = 32000); *parallel* λ_{max} = 316 nm (ε = 43000). – ^{1}H NMR ($CDCl_3$, 300 MHz) δ *antiparallel* = 1.67 (3 H, s), 1.91 (6 H, d, *J* = 1.2 Hz), 2.03 (6 H, s), 2.33 (3 H, s), 6.40 (2 H, q, *J* = 1.2 Hz); *parallel* = 1.73 (3 H, s), 1.82 (6 H, d, *J* = 1.2 Hz), 2.04 (6 H, s), 2.32 (3 H, s), 6.37 (2 H, q, *J* = 1.2 Hz). – ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ *antiparallel* = 12.89 (2-CH_3), 15.02 (4-CH_3, 6-CH_3), 15.37 (4'-CH_3, 4''-CH_3), 16.70 (5-CH_3), 106.54 (C5', C5''), 131.61 (C2), 134.68 (C1, C3), 136.06 (C4, C6), 136.25 (C5), 139.72 (C4', C4''), 188.45 (C2', C2''); *parallel* = 12.97 (2-CH_3), 15.16 (4-CH_3, 6-CH_3), 15.35 (4'-CH_3, 4''-CH_3), 16.73 (5-CH_3), 106.37 (C5', C5''), 131.85 (C2), 134.74 (C1, C3), 136.11 (C4, C6), 136.48 (C5), 138.43 (C4', C4''), 188.59 (C2', C2''). – CTA (EtOH 95%): *antiparallel k*'(+) = 0.25; *k*'(–) = 0.25; *parallel k*' = 0.15.

1,3-Bis(4,5-dimethyl-2-thioxo-3-thiazolinyl)-2,4,5,6-tetramethylbenzene (3b): Yield: 36% – $C_{20}H_{24}N_2S_4$ (420): calcd. C 57.14, H 5.71, N 6.67, S 30.48; found C 57.32, H 6.02, N 5.79, S 30.54. – UV (MeOH): *antiparallel* λ_{max} = 318 nm (ε = 30000); *parallel* λ_{max} = 316 nm (ε = 42000). – ^{1}H NMR ($CDCl_3$, 300 MHz) δ *antiparallel* = 1.69 (3 H, s), 1.82 (6 H, q, *J* = 0.8 Hz), 2.04 (6 H, s), 2.23 (6 H, q, *J* = 0.8 Hz), 2.33 (3 H, s); *parallel* = 1.72 (6 H, q, *J* = 0.9 Hz), 1.76 (3 H, s), 2.05 (6 H, s), 2.22 (6 H, q, *J* = 0.9 Hz), 2.32 (3 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ *antiparallel* = 11.92 (5'-CH_3, 5''-CH_3), 12.91 (4'-CH_3, 4''-CH_3), 13.04 (2-CH_3),

15.13 (4-CH_3, 6-CH_3), 16.75 (5-CH_3), 118.19 (C5', C5''), 131.62 (C2), 134.58 (C4', C4''), 135.60 (C1, C3), 135.92 (C4, C6), 136.08 (C5), 186.21 (C2', C2''); *parallel* = 11.99 (5'-CH_3, 5''-CH_3), 12.87 (4'-CH_3, 4''-CH_3), 13.08 (2-CH_3), 15.26 (4-CH_3, 6-CH_3), 16.79 (5-CH_3), 118.02 (C5', C5''), 131.63 (C2), 133.21 (C4', C4''), 135.46 (C1, C3), 135.93 (C4, C6), 136.23 (C5), 186.41 (C2', C2''). – CTA (EtOH 95%): *antiparallel k*'(+) = 0.10; *k*'(–) = 0.10; *parallel k*' = 0.02.

2-Methyl-1,3-bis(4-methyl-2-thioxo-3-thiazolinyl)-5-isopropylbenzene (4a): Yield: 70% – $C_{18}H_{20}N_2S_4$ (392): calcd. C 55.10, H 5.10, N 7.14, S 32.65; found C 55.40, H 5.53, N 7.35, S 32.75. – UV (MeOH): *antiparallel* λ_{max} = 316 nm (ε = 26000); *parallel* λ_{max} = 314 nm (ε = 14000). – ^{1}H NMR ($CDCl_3$, 300 MHz) δ *antiparallel* = 1.29 (6 H, d, *J* = 6.9 Hz), 1.74 (3 H, s), 1.95 (6 H, d, *J* = 1.1 Hz), 3.02 (1 H, h, *J* = 6.9 Hz), 6.38 (2 H, q, *J* = 1.1 Hz), 7.15 (2 H, s); *parallel* = 1.29 (6 H, d, *J* = 6.8 Hz), 1.81 (3 H, s), 1.87 (6 H, d, *J* = 1.0 Hz), 3.02 (1 H, h, *J* = 6.9 Hz), 6.36 (2 H, q, *J* = 1.1 Hz), 7.18 (2 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ *antiparallel* = 12.29 (2-CH_3), 15.93 (4'-CH_3, 4''-CH_3), 23.39 [$CH(CH_3)_2$], 23.88 [$CH(CH_3)_2$], 33.37 [$CH(CH_3)_2$], 106.54 (C5', C5''), 127.68 (C4, C6), 132.66 (C2), 138.36 (C1, C3), 140.03 (C4', C4''), 149.87 (C5), 189.22 (C2', C2''); *parallel* = 12.31 (2-CH_3), 15.81 (4'-CH_3, 4''-CH_3), 23.67 [$CH(CH_3)_2$], 33.39 [$CH(CH_3)_2$], 106.6 (C5', C5''), 128.08 (C4, C6), 132.69 (C2), 138.37 (C1, C3), 138.74 (C4', C4''), 149.79 (C5), 189.36 (C2', C2''). – CTA (EtOH 95%): *antiparallel k*'(–) = 0.31; *k*'(+) = 0.31; *parallel k*' = 0.37.

1,3-Bis(4,5-dimethyl-2-thioxo-3-thiazolinyl)-2-methyl-5-isopropylbenzene (4b): Yield: 25% – $C_{20}H_{24}N_2S_4$ (420): calcd. C 57.14, H 5.71, N 6.67, S 30.48; found C 57.39, H 5.85, N 6.85, S 30.62. – UV (MeOH): *antiparallel* λ_{max} = 320 nm (ε = 37000); *parallel* λ_{max} = 322 nm (ε = 18000). – ^{1}H NMR ($CDCl_3$, 300 MHz) δ *antiparallel* = 1.29 (6 H, d, *J* = 6.9 Hz), 1.77 (3 H, s), 1.86 (6 H, q, *J* = 0.7 Hz), 2.21 (6 H, q, *J* = 0.7 Hz), 2.99 (1 H, h, *J* = 6.9 Hz), 7.13 (2 H, s); *parallel* = 1.28 (6 H, d, *J* = 6.9 Hz), 1.76 (6 H, q, *J* = 0.9 Hz), 1.83 (3 H, s), 2.20 (6 H, q, *J* = 0.9 Hz), 3.0 (1 H, h, *J* = 6.9 Hz), 7.16 (2 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ *antiparallel* = 11.73 (5'-CH_3, 5''-CH_3), 12.33 (2-CH_3), 13.41 (4'-CH_3, 4''-CH_3), 23.29 [$CH(CH_3)_2$], 23.86 [$CH(CH_3)_2$], 33.31 [$CH(CH_3)_2$], 118.05 (C5', C5''), 127.47 (C4, C6), 132.58 (C2), 134.78 (C1, C3), 139.12 (C4', C4''), 149.61 (C2), 186.99 (C2', C2''). – CTA (EtOH 95%): *antiparallel k*'(–) = 0.16; *k*'(+) = 0.16; *parallel k*' = 0.06.

General Procedure for the Synthesis of the Oxygenated Compounds (Thione-ones 5a,b–8a,b and Bis-ones 9a,b–12a,b): This procedure is an adaptation of the method used by Roussel et al.[5] for the preparation of mono(oxothiazolinyl) aromatic compounds from the corresponding mono(thioxothiazolinyl) aromatic compounds.

a) Preparation of the Thiazolinium Salt: To one mmol of bis-thione dissolved in the minimum volume of anhydrous acetone was added methyl iodide (0.6 mL, 10 mmol), and the reaction left at room temperature, in a closed vessel, until all the bis-thione was consumed. The reaction was monitored by TLC (eluent $CHCl_3$/AcOEt, 9:1, UV λ = 254 nm); the thiazolinium salt formed is not eluted. If the salt crystallized it was isolated by filtration; if it remained in solution it was recovered by evaporating the acetone.

b) Transformation of the Mono and/or the Bis(thiazolinium) Salt into the Corresponding Thione-one or Bis-one: A mixture of the thiazolinium salt with 8 mmol of sodium methoxide in methanol was stirred for 24–48 hours at room temperature. After the completion of the reaction [monitored by TLC (silica, eluent $CHCl_3$/AcOEt, 9:1)], 350 mL of water was added. There were two cases: either the oxygenated product precipitated and was separated by filtration or the oxygenated product formed an emulsion which was extracted with 3 × 50 mL of dichloromethane; the solution was then dried on sodium sulfate and the solvent evaporated. In both cases, the obtained product could be the thione-one, the bis-one, or a mixture of the two with the initial bis-thione. The product was purified by liquid chromatography on silica (eluent $CHCl_3$/AcOEt, 9:1). Yields for the oxygenated products varied between 20% and 75%. The starting materials used were either the pure conformers of the bis-(thioxothiazolinyl) aromatic compounds, or the mixture of *antiparallel* and *parallel* conformers. The reaction should preferably be performed with pure conformers in order to separate the products more easily. NMR data of **7a**, **8a**, **8b**, **12a** and **12b**: *Assignments made on a mixture *antiparallel* thione-one and *antiparallel* bis-one.

2-Methyl-3-(4-methyl-2-oxo-3-thiazolinyl)-1-(4-methyl-2-thioxo-3-thiazolinyl)benzene (5a): $C_{15}H_{14}N_2S_3O$ (334): calcd. C 53.89; H 4.19; N 8.38; S 28.74; found C 53.99; H 4.01; N 8.32; S 28.75. – m.p. (°C): *antiparallel* 242–244 °C; *parallel* 205–207 °C. – R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.33; *parallel* 0.17. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.87 (3 H, s); 1.85 (3 H, d, *J* = 1.3 Hz), 1.97 (3 H, d, *J* = 1.2 Hz), 5.92 (1 H, q, *J* = 1.3 Hz), 6.39 (1 H, q, *J* = 1.2 Hz), 7.25 (1 H, dd, *J* = 7.8 Hz and *J* = 1.2 Hz), 7.38 (1 H, dd, *J* = 8 Hz and *J* = 8 Hz), *parallel* = 1.79 (3 H, d, *J* = 1.3 Hz), 1.86 (3 H, d, *J* = 1.2 Hz), 1.91 (3 H, s); 5.92 (1 H, q, *J* = 1.3 Hz), 6.36 (1 H, q, *J* = 1.2 Hz), 7.30 (1 H, dd, *J* = 7.9 Hz and *J* = 8.2 Hz), 7.37 (1 H, dd, *J* = 8.2 Hz and *J* = 1.2 Hz), 7.52 (1 H, t, *J* = 7.9 Hz and *J* = 8.2 Hz). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel* = 12.66 (2-CH_3), 15.62 (4''-CH_3), 15.95 (4'-CH_3), 96.79 (C5''), 106.74 (C5'), 128.31 (C5), 129.41 (C4), 130.67 (C6), 132.68 (C4''), 136.43 (C2), 136.86 (C3), 138.33 (C1), 139.69 (C4'), 172.03 (C2''), 189.44 (C2'); *parallel* = 12.59 (2-CH_3), 15.50 (4''-CH_3), 15.73 (4'-CH_3), 97.09 (C5''), 106.66 (C5'), 128.15 (C5), 129.86 (C4), 130.83 (C6), 131.22 (C4''), 138.31 (C1), 138.89 (C4'), 172.66 (C2''), 190.00 (C2').

3-(4,5-Dimethyl-2-oxo-3-thiazolinyl)-1-(4,5-dimethyl-2-thioxo-3-thiazolinyl)-2-methylbenzene (5b): $C_{17}H_{18}N_2S_3O$ (362): calcd. C 56.35; H 4.97; N 7.73; S 26.52; found C 56.58; H 5.10; N 7.75; S 26.69. – m.p.: *antiparallel* 243–245 °C; *parallel* 222–224 °C. – R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.32; *parallel* 0.15. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.76 (3 H, q, *J* = 0.9 Hz), 1.86 (3 H, q, *J* = 0.85 Hz), 1.88 (3 H, s); 2.15 (3 H, q, *J* = 0.9 Hz), 2.21 (3 H, q, *J* = 0.85 Hz), 7.23 (1 H, dd, *J* = 7.9 Hz and *J* = 1.1 Hz), 7.35 (1 H, dd, *J* = 7.9 Hz and *J* = 1.1 Hz), 7.49 (1 H, t, *J* = 7.9 Hz), *parallel* = 1.69 (3 H, q, *J* = 1 Hz), 1.76 (3 H, q, *J* = 0.9 Hz), 1.92 (3 H, s); 2.15 (3 H, q, *J* = 1 Hz), 2.20 (3 H, q, *J* = 0.9 Hz), 7.27 (1 H, dd, *J* = 7.8 Hz and *J* = 0.9 Hz), 7.34 (1 H, dd, *J* = 7.8 Hz and *J* = 0.9 Hz), 7.48 (1 H, t, *J* = 7.8 Hz). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel* = 11.82 (5'-CH_3), 12.14 (4''-CH_3), 12.28 (5''-CH_3), 12.71 (4'-CH_3), 13.42 (2-CH_3), 107.64 (C5''), 118.26 (C5'), 126.98 (C4''), 128.13 (C5), 129.18 (C4), 130.54 (C6), 134.46 (C4'), 136.40 (C3), 137.50 (C1), 139.09 (C2), 171.00 (C2''), 187.19 (C2'); *parallel* = 11.87 (5'-CH_3), 12.01 (4''-CH_3), 12.33 (5''-CH_3), 12.72 (4'-CH_3), 13.21 (2-CH_3), 107.95 (C5''), 118.15 (C5'), 125.82 (C4''), 128.03 (C5), 129.77 (C4), 130.81 (C6), 133.49 (C4'), 136.35 (C3), 137.56 (C1), 139.28 (C2), 170.31 (C2''), 187.50 (C2').

4,5,6-Trimethyl-3-(4-methyl-2-oxo-3-thiazolinyl)-1-(4-methyl-2-thioxo-3-thiazolinyl)benzene (6a): R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.61; *parallel* 0.27. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.88 (3 H, d, *J* = 1.3 Hz), 1.95 (3 H, d, *J* = 1.2 Hz), 2.03 (3 H, s); 2.15 (3 H, s), 2.35 (3 H, s), 5.88 (1 H, q, *J* = 1.3 Hz), 6.36 (1 H, q, *J* = 1.2 Hz), 6.88 (1 H, s), *parallel* = 1.80 (3 H, d, *J* = 1.1 Hz), 1.87 (3 H, d, *J* = 1.0 Hz), 2.04 (3 H, s); 2.14 (3 H, s), 2.35 (3 H, s), 5.88 (1 H, q, *J* = 1.1 Hz), 6.33 (1 H, q, *J* = 1.0 Hz), 6.89 (1 H, s).

3-(4,5-Dimethyl-2-oxo-3-thiazolinyl)-1-(4,5-dimethyl-2-thioxo-3-thiazolinyl)-4,5,6-trimethylbenzene (6b): m.p.: *antiparallel* 216–217 °C; *parallel* 185–187 °C. – R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.61; *parallel* 0.27. – ^1H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.78 (3 H, q, J = 0.9 Hz), 1.85 (3 H, q, J = 0.8 Hz), 2.03 (3 H, s); 2.13 (3 H, s), 2.15 (3 H, q, J = 0.9 Hz), 2.20 (3 H, q, J = 0.8 Hz), 2.33 (3 H, s), 6.85 (1 H, s); *parallel* = 1.71 (3 H, q), 1.77 (3 H, q), 2.04 (3 H, s); 2.13 (3 H, s), 2.15 (3 H, q), 2.18 (3 H, q), 2.33 (3 H, s), 6.85 (1 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel* = 11.81 (5'-CH_3), 12.27 (5''-CH_3), 12.34 (4''-CH_3), 13.41 (4'-CH_3), 14.78 (6-CH_3), 15.05 (4-CH_3), 16.96 (5-CH_3), 107.19 (C5''), 117.91 (C5'), 126.35 (C2), 127.36 (C4''), 139.27 (C5), 134.12 (C3), 134.97 (C4'), 135.58 (C1), 135.81 (C6), 137.23 (C4), 171.16 (C2''), 187.34 (C2').

2,4,5,6-Tetramethyl-3-(4-methyl-2-oxo-3-thiazolinyl)-1-(4-methyl-2-thioxo-3-thiazolinyl)benzene (7a): $C_{18}H_{20}N_2S_3O$ (376): calcd. C 57.45; H 5.32; N 7.45; S 25.53; found C 57.70; H 5.20; N 7.49; S 25.80. – m.p.: *parallel* 250–256 °C. – R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.44; *parallel* 0.21. – ^1H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.74 (3 H, s), 1.78 (3 H, d, J = 1.3 Hz), 1.91 (3 H, d, J = 1.2 Hz), 2.01 (3 H, s); 2.12 (3 H, s), 2.31 (3 H, s), 5.94 (1 H, q, J = 1.3 Hz), 6.41 (1 H, q, J = 1.2 Hz); *parallel* = 1.72 (3 H, d, J = 1.3 Hz), 1.79 (3 H, s), 1.82 (3 H, d, J = 1.1 Hz), 2.01 (3 H, s); 2.11 (3 H, s), 2.30 (3 H, s), 5.94 (1 H, q, J = 1.3 Hz), 6.37 (1H, q, J = 1.1 Hz). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel** = 13.08 (2-CH_3), 15.08 (6-CH_3), 15.18 (4-CH_3), 15.33 (4''-CH_3), 15.55 (4'-CH_3), 16.81 (5-CH_3), 96.69 (C5''), 106.61 (C5'), 132.50 (C4'), 137.27 (C5), 139.70 (C4'), 171.74 (C2''), 188.74 (C2').

3-(4,5-Dimethyl-2-oxo-3-thiazolinyl)-1-(4,5-dimethyl-2-thioxo-3-thiazolinyl)-2,4,5,6-tetramethylbenzene (7b): m.p.: *antiparallel* 181–183 °C. – R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.52. – ^1H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.69 ppm (3 H, q, J = 0.8 Hz), 1.76 (3 H, s), 1.81 (3 H, q, J = 0.7 Hz), 2.0 (3 H, s), 2.12 (3 H, s); 2.16 (3 H, q, J = 0.8 Hz), 2.22 (3 H, q, J = 0.7 Hz), 2.29 (3 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel* = 11.66 (4''-CH_3), 11.93 (5'-CH_3), 12.39 (5''-CH_3), 12.98 (4'-CH_3), 13.15 (2-CH_3), 15.07 (6-CH_3), 15.33 (4-CH_3), 16.76 (5-CH_3), 107.59 (C5''), 118.13 (C5'), 126.92 (C4''), 132.35 (C2), 133.68 (C3), 134.36 (C4'), 135.31 (C1), 135.47 (C4), 135.86 (C6), 137.07 (C5), 170.72 (C2''), 186.46 (C2').

2-Methyl-3-(4-methyl-2-oxo-3-thiazolinyl)-1-(4-methyl-2-thioxo-3-thiazolinyl)-5-isopropylbenzene (8a): m.p.: *antiparallel* 181–183 °C. – R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.47. – ^1H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.29 (6 H, d, J = 7 Hz), 1.81 (3 H, s), 1.83 (3 H, d, J = 1.4 Hz), 1.96 (3 H, d, J = 1.1 Hz), 2.99 (1 H, sept, J = 7 Hz); 5.89 (1 H, q, J = 1.4 Hz), 6.37 (1 H, q, J = 1.1 Hz), 7.10 (1 H, s), 7.21 (1 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel** = 12.25 (2-CH_3), 15.55 (4''-CH_3), 15.89 (4'-CH_3), 23.32 [$CH(CH_3)_2$], 23.85 [$CH(CH_3)_2$], 33.32 [$CH(CH_3)_2$], 96.45 (C5''), 106.37 (C5'), 127.31 (C4), 128.43 (C6), 132.77 (C4''), 133.13 (C2), 136.53 (C3), 138.00 (C1), 139.74 (C4'), 149.39 (C5), 171.89 (C2''), 189.31 (C2').

3-(4,5-Dimethyl-2-oxo-3-thiazolinyl)-1-(4,5-dimethyl-2-thioxo-3-thiazolinyl)-2-methyl-5-isopropylbenzene (8b): R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.6. – ^1H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.27 (6 H, d, J = 6.9 Hz), 1.74 (3 H, q, J = 0.8 Hz), 1.83 (3 H, s), 1.86 (3 H, q, J = 0.7 Hz), 2.14 (3 H, q, J = 0.8 Hz), 2.21 (3 H, q, J = 0.7 Hz), 2.94 (1 H, h, J = 6.9 Hz); 7.07 (1 H, s), 7.18 (1 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel** = 11.86 (5'-CH_3), 12.24 (4''-CH_3), 12.32 (5''-CH_3), 12.43 (2-CH_3), 13.57 (4'-CH_3), 23.88 [$CH(CH_3)_2$], 24.00 [$CH(CH_3)_2$], 33.39 [$CH(CH_3)_2$], 107.40 (C5''), 118.02 (C5'), 126.96 (C4'), 127.22 (C6), 128.45 (C4), 133.09 (C2), 134.62 (C1), 137.11 (C3), 138.70 (C4'), 149.26 (C5), 170.97 (C2''), 187.20 (C2').

2-Methyl-1,3-bis(4-methyl-2-oxo-3-thiazolinyl)benzene (9a): m.p.: *parallel* 252–253 °C. – R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.35; *parallel* 0.08. – ^1H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.85 (6 H, d, J = 1.2 Hz), 1.93 (3 H, s); 5.92 (2 H, q, J = 1.2 Hz), 7.31 (2 H, d, J = 8 Hz), 7.46 (1 H, t, J = 8 Hz), *parallel* = 1.77 (6 H, d, J = 1.4 Hz), 1.95 (3 H, s); 5.92 (2 H, q, J = 1.4 Hz), 7.33 (2 H, d, J = 7.4 Hz), 7.46 (1 H, t, J = 7.4 Hz). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel* = 12.66 (2-CH_3); 15.62 (4'-CH_3, 4''-CH_3), 96.79 (C5', C5''), 127.83 (C5), 130.17 (C4, C6), 132.40 (C4', C4''), 136.43 (C1, C3), 136.86 (C2), 172.03 (C2', C2''); *parallel* = 12.61 (2-CH_3); 15.44 (4'-CH_3, 4''-CH_3), 97.03 (C5', C5''), 127.78 (C5), 130.49 (C4, C6), 131.52 (C4', C4''), 136.50 (C1, C3), 136.74 (C2), 171.38 (C2', C2''). – CTA (EtOH 95%): *antiparallel* k'(+) = 0.12; k'(–) = 0.12.

1,3-Bis(4,5-dimethyl-2-oxo-3-thiazolinyl)2-methylbenzene (9b): R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.34. – ^1H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.75 (6 H, q, J = 0.9 Hz), 1.94 (3 H, s); 2.15 (6 H, q, J = 0.9 Hz), 7.27 (2H, d, J = 7.9 Hz), 7.42 (1 H, t, J = 7.9 Hz), *parallel* = 1.67 (6 H, q, J = 1 Hz), 1.96 (3 H, s); 2.14 (6 H, q, J = 1 Hz), 7.29 (2H, d, J = 7.4 Hz), 7.42 (1 H, t, J = 7.4 Hz). – CTA (EtOH 95%): *antiparallel* k'(+) = 0.06; k'(–) = 0.06.

4,5,6-Trimethyl-1,3-bis(4-methyl-2-oxo-3-thiazolinyl)benzene (10a): R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.3; *parallel* 0.2. – ^1H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.85 ppm (6 H, d, J = 1.3 Hz), 2.11 (6 H, s), 2.32 (3 H, s), 5.88 (2H, q, J = 1.3 Hz), 6.90 (1 H, s), *parallel* = 1.80 (3 H, d, J = 1.2 Hz), 2.11 (6 H, s), 2.32 (3 H, s); 5.88 (2H, q, J = 1.2 Hz), 6.90 (1 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel* = 14.92 (4'-CH_3, 4''-CH_3), 15.64 (4-CH_3, 6-CH_3), 16.95 (5-CH_3), 96.24 (C5', C5''), 126.47 (C2), 132.78 (C4', C4''), 133.00 (C1, C3), 136.82 (C4, C6), 139.29 (C5), 172.25 (C2', C2''); *parallel* = 15.02 (4'-CH_3, 4''-CH_3), 15.71 (4-CH_3, 6-CH_3), 17.00 (5-CH_3), 96.64 (C5', C5''), 126.48 (C2), 131.94 (C4', C4''), 133.17 (C1, C3), 137.10 (C4, C6), 139.16 (C5), 171.53 (C2', C2''). – CTA (EtOH 95%): *antiparallel* k'(+) = 0.64; k'(–) = 0.64; *parallel* k' = 0.50.

1,3-Bis(4,5-dimethyl-2-oxo-3-thiazolinyl)-4,5,6-trimethylbenzene (10b): m.p.: *antiparallel* 192–194 °C; *parallel* 205–207 °C. – R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.53; *parallel* 0.12. – ^1H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.74 (6 H, q, J = 0.7 Hz), 2.11 (6 H, s), 2.13 (6 H, q, J = 0.7 Hz), 2.30 (3 H, s), 6.86 (1 H, s), *parallel* = 1.69 (6 H, q, J = 0.8 Hz), 2.11 (6 H, s), 2.13 (6 H, q, J = 0.8 Hz), 2.31 (3 H, s), 6.87 (1 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel* = 12.24 (5'-CH_3, 5''-CH_3), 12.29 (4'-CH_3, 4''-CH_3), 14.98 (4-CH_3, 6-CH_3), 16.97 (5-CH_3), 107.13 (C5', C5''), 126.65 (C2), 127.11 (C4', C4''), 133.71 (C1, C3), 136.67 (C4, C6), 139.07 (C5), 171.24 (C2', C2''); *parallel* 12.27 (5'-CH_3, 5''-CH_3), 12.39 (4'-CH_3, 4''-CH_3), 15.07 (4-CH_3, 6-CH_3), 17.00 (5-CH_3), 107.44 (C5', C5''), 126.27 (C2), 126.53 (C4', C4''), 133.73 (C1, C3); 136.87 (C4, C6), 138.90 (C5), 170.57 (C2', C2''). – CTA (EtOH 95%): *antiparallel* k'(+) = 0.40; k'(–) = 0.76; *parallel* k' = 0.38.

2,4,5,6-Tetramethyl-1,3-bis(4-methyl-2-oxo-3-thiazolinyl)benzene (11a): m.p.: *parallel* 288–289 °C. – R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.49; *parallel* 0.15. – ^1H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.77 (6 H, d, J = 1.3 Hz), 1.82 (3 H, s), 2.09 (6 H, s); 2.28 (3 H, s), 5.94 (2H, q, J = 1.3 Hz), *parallel* = 1.70 (6 H, d, J = 1.2 Hz), 1.84 (3 H, s), 2.08 (6 H, s); 2.28 (3 H, s), 5.94 (2H, q, J = 1.2 Hz). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel* = 13.13 ppm (2-CH_3), 15.06 (4'-CH_3, 4''-CH_3), 15.16 (4-CH_3, 6-CH_3), 16.78 (5-CH_3), 96.66 (C5', C5''), 132.43 (C4', C4''), 132.50 (C1, C3), 132.71 (C2), 135.93 (C5), 136.86 (C4, C6), 171.76 (C2', C2''); *parallel* = 13.21

(2-CH_3), 15.14 (4'-CH_3, 4''-CH_3), 15.27 (4-CH_3, 6-CH_3), 16.80 (5-CH_3), 96.99 (C5', C5''), 131.01 (C4', C4''), 131.57 (C1, C3), 132.69 (C2), 135.79 (C5), 137.04 (C4, C6), 171.17 (C2', C2''). – CTA (EtOH 95%): *antiparallel* $k'(+) = 0.34$; $k'(-) = 0.34$.

1,3-Bis(4,5-dimethyl-2-oxo-3-thiazolinyl)-2,4,5,6-tetramethylbenzene (11b): m.p.: *antiparallel* 181–183 °C. – R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.52. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.69 (6 H, q, J = 0.7 Hz), 1.83 (3 H, s), 2.08 (6 H, s), 2.16 (6 H, q, J = 0.7 Hz), 2.26 (3 H, s); *parallel* = 1.61 (6 H, q, J = 0.8 Hz), 1.85 (3 H, s), 2.08 (6 H, s), 2.16 (6 H, q, J = 0.8 Hz), 2.27 (3 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel* = 11.69 (4'-CH_3, 4''-CH_3), 12.41 (5'-CH_3, 5''-CH_3), 13.24 (2-CH_3), 15.28 (4-CH_3, 6-CH_3), 16.76 (5-CH_3), 107.55 (C5', C5''), 126.74 (C4', C4''), 133.12 (C2), 133.42 (C1, C3), 135.69 (C5), 136.69 (C4, C6), 170.74 (C2', C2''). – CTA (EtOH 95%): *antiparallel* $k'(+) = 0.14$; $k'(-) = 0.14$

5-Isopropyl-2-methyl-1,3-bis(4-methyl-2-oxo-3-thiazolinyl)benzene (12a): R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.4; *parallel* 0.11. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.26 (6 H, d, J = 6.9 Hz), 1.84 (6 H, d, J = 1.3 Hz), 1.88 (3 H, s), 2.95 (1 H, h, J = 6.9 Hz); 5.89 (2H, q, J = 1.3 Hz), 7.14 (1 H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel** = 12.42 (2-CH_3), 15.76 (4'-CH_3, 4''-CH_3), 23.42 [$CH(CH_3)_2$], 24.04 [$CH(CH_3)_2$], 33.40 [$CH(CH_3)_2$], 96.59 (C5', C5''), 128.18 (C4, C6), 132.63 (C4', C4''), 133.55 (C3), 136.12 (C1, C3), 148.94 (C5), 172.04 (C2', C2''). – CTA (EtOH 95%): *antiparallel* $k'(+) = 0.28$; $k'(-) = 0.28$.

1,3-Bis(4,5-dimethyl-2-oxo-3-thiazolinyl)-5-isopropyl-2-methylbenzene (12b): R_f ($CHCl_3$/AcOEt, 9:1): *antiparallel* 0.54. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ *antiparallel* = 1.27 (6 H, d, J= 6.9 Hz), 1.74 (6 H, q, J = 1.1 Hz), 1.84 (3 H, s), 2.14 (6 H, q, J = 1.1 Hz), 2.97 (1 H, h, J = 6.9 Hz), 7.11 (2H, s), *parallel* = 1.26 (6 H, d, J= 6.9 Hz), 1.66 (6 H, q, J = 0.7 Hz), 1.90 (3 H, s), 2.14 (6 H, q, J = 0.7 Hz), 2.94 (1 H, h, J = 6.9 Hz), 7.13 (2H, s). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ *antiparallel** = 12.22 (4'-CH_3, 4''-CH_3), 12.32 (5'-CH_3, 5''-CH_3), 12.47 (2-CH_3), 23.38 [$CH(CH_3)_2$], 24.00 [$CH(CH_3)_2$], 33.39 [$CH(CH_3)_2$], 107.45 (C5', C5''), 126.94 (C4', C4''), 128.03 (C4, C6), 133.70 (C2), 137.30 (C1, C3), 148.71 (C5), 170.93 (C2', C2''). – CTA (EtOH 95%): *antiparallel* $k'(+) = 0.21$; $k'(-) = 0.21$.

[1] S. M. Heilman, L. R. Krepski, J. K.Rasmussen, A. R. Katritzky, R. D. Tarr, Eur. Pat. Appl. Appl. EP 239,369 (Cl C07D277/36), 26p., cf. *Chem. Abstr*. **1988**, *108*, P195821x.

[2] A. R. Katritzky, R. D. Tarr, S. M. Heilman, J. K. Rasmussen, L. R. Krepski, *J. Polym. Sci.: Part. A: Polym. Chem*. **1987**, *25*, 3205–3214.

[3] D. Gust, *J. Am. Chem. Soc*. **1977**, *99*, 6980–6982.

[4] D. Gust, A. Patton, *J. Am. Chem. Soc*. **1978**, *100*, 8175–8181.

[5] A.Patton, J. Wang Dirks, D. Gust, *J. Org. Chem*. **1979**, *44*, 4749–4757.

[6] R. H. Mitchell, J. Shue-Hen Jan, *Can. J. Chem*. **1980**, *58*, 2584–2588.

[7] R. L. Huang, *J. Chem. Soc*. **1954**, 3655–3658.

[8] R. L. Huang, *J. Chem. Soc*. **1959**, 923–928.

[9] G. R. Newkome, J. M. Roper, J. M. Robinson, *J. Org. Chem*. **1980**, *45*, 4380–4385.

[10] E. Hammerschmidt, F. Vögtle, *Chem. Ber*. **1980**, *113*, 1121–1124.

[11] Yee-Hing Lai, Pu Cheng, *J. Chem. Soc*., *Perkin Trans. 2* **1989**, *11*, 1665.

[12] P. J. Marriott, Yee-Hing Lai, *J. Chromatogr*. **1988**, *447*, 29.

[13] Yee-Hing Lai, *J. Chem. Soc*., *Perkin Trans. 2* **1986**, 1667.

[14] M. W. Fagan, D. Gust, *J. Org. Chem*. **1981**, *46*, 1499–1500.

[15] D. Gust, M. W. Fagan, *J. Org. Chem*. **1980**, *45*, 2511–2512.

[16] J. A. Zoltewicz, N. M. Maier, W. M. F. Fabian, *J. Org. Chem*. **1997**, *62*, 3215–3219.

[17] J. A. Zoltewicz, N. M. Maier, W. M. F. Fabian, *J. Org. Chem*. **1997**, *62*, 2763–2766.

[18] C. Roussel, J.L. Stein, F. Beauvais, *New J. Chem*. **1990**, *14*, 169–173.

[19] C. Popescu, Ph.D. Dissertation, Université d'Aix-Marseille III, **1994**.

[20] J. Garín, E. Meléndez, F. L. Merchan, P. Merino, T. Tejero, *Bull. Soc. Chim. Belg*. **1988**, *97(10)*, 791–792.

[21] C. Kashima, A. Katoh A, *J. Chem. Soc., Perkin Trans. 1* **1980**, 1599–1602.

[22] Y. Okamoto, D. Dimberger, T. Burgermeister, G. Dannhardt, W. Wiegrebe, *Arch. Pharm. (Weinheim)* **1986**, *319*, 1122–1129.

[23] B. Blessington, A. Beiraghi, *J. Chromatogr*. **1990**, *522*, 195–203.

[24] K. Brenauer, F. Gretillat, *Helv. Chim. Acta* **1989**, *72*, 477–481.

[25] S. P. Pappas, B. C. Pappas, Y. Okamoto, H. Sakamoto, *J. Org. Chem*. **1988**, *53*, 4404.

[26] TSAR 3.0 software from Oxford Molecular Group (Silicon Graphics station 02R10000).

[27] C. Roussel, M. Adjimi, A. Chemlal, *J. Org. Chem*. **1988**, *53*, 5076–5080.

[28] C. Roussel, J. L. Stein, M. Sergent, R. Phan Tan Luu, *Recent Advances in Chiral Separations* (Eds.: D. Stevenson, I. D. Wilson), Plenum Press, **1990**, p. 105–108.

[29] C. Roussel, S. Lehuede, C. Popescu, J. L. Stein, *Chirality* **1993**, *5*, 207–212.

[30] C. Roussel, A. Favrou, *Chirality* **1993**, *5*, 471–478.

[31] C. Roussel, A. Favrou, *J. Incl. Phen.* **1993**, *16*, 283–296.

[32] C. Roussel, C. Popescu, *Chirality* **1994**, *6*, 251–260.

[33] C. Roussel, C. Popescu, T. Shibata, *J. Chromatogr. A* **1996**, *722*, 177–188.

Received July 19, 1999
[O99419]