Conformational properties of 3,3′-, 3,4′- and 4,4′-dimethyl- and -bis(methylsulfanyl)-2,2′-bithiophenes

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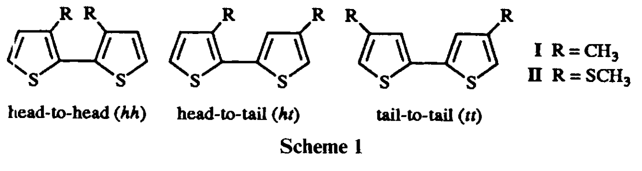
The conformational properties of the title compounds, which are the basic head-to-head, head-to-tail and tail-to-tail repeat units of regioregular poly(3-methylthiophenes) and poly[3-(methylsulfanyl)thiophenes], are discussed. The paper reports the X-ray structures of the two 4,4′- derivatives, ^{1}H NMR NOE data on the 3,4′- and 4,4′- derivatives and force field MM2 calculations of the conformation of the three bis(methylsulfanyl) derivatives.

Functionalized oligo- and poly-thiophenes are soluble and processable materials of great current interest for applications in the field of electronic and electrooptical devices.[1].

A detailed knowledge of the effects of the substituents and of the regiochemistry of substitution on the conformational properties of these materials in the solid phase and in solution is of great importance since it forms the basis for the control and the tuning of their electric and optical properties. Indeed, the conformation of oligo- and poly-thiophenes—in single crystals, in ordered films or in solution—governs the degree of π-overlap between adjacent rings and the band gap between ground and excited molecular states, hence it determines all electrical and optical properties which are of interest to the industrial application of these materials.[1]

Knowledge of the conformational properties of oligo- and poly-thiophenes is scarce, despite the large number of papers published on these materials during the last decade. The energy barriers to rotation around the carbon–carbon bond that links two adjacent rings are low, and freezing of the conformational equilibria existing in solution would require low temperatures which cannot be attained with routine NMR instruments. Moreover, oligothiophenes are difficult to crystallize and only a few complete single crystal X-ray characterizations have been reported so far.[2,3] Comparison of data in the solid phase and in solution indicates that the conformation of substituted oligothiophenes in the solid state is different—generally more planar—from that in solution and depends on the interactions among substituents which, in turn, are related to the regiochemistry of substitution.[2g–i] Several *ab initio*, semi-empirical and force field calculations of the conformation of β-substituted 2,2′-bithiophenes have been published in recent years, indicating that the inter-ring twist angle and the conformation of these compounds are modulated by the regiochemistry of substitution.[4–6] The present paper reports NMR and UV data on the three α-conjugated regioisomers of dimethyl- and bis(methylsulfanyl)-2,2′-bithiophene having the thiophene rings linked head-to-head (*hh*), head-to-tail (*ht*) and tail-to-tail (*tt*) (Scheme 1) as well as the X-ray structures of the two tail-to-tail derivatives, which give single crystals suitable for X-ray analysis. The *hh*, *ht* and *tt* regioisomers represent the basic repeat units of the regioregular head-to-tail and head-to-head/tail-to-tail versions of poly(3-methylthiophene) and poly[3-(methylsulfanyl)thiophene], currently under study in our laboratory, and the knowledge of their electronic and conformational properties is fundamental for the comprehension of the properties of the polymers. This paper also gives the results of MM2 force field calculations of the conformations of the bis(methylsulfanyl) derivatives, **II**. MM2 calculations of the conformations of the dimethyl derivatives **I** have been previously reported by us as a part of a study concerning the electropolymerization of these dimers and aimed at obtaining regiochemically different versions of poly(3-methylthiophene) with different electrochromic properties.[6c]



Scheme 1

Results

Crystal structures of compounds I*tt* and II*tt*

Figs. 1 and 2 show the molecular structures of I*tt* and II*tt*, respectively, along with atom numbering schemes, bond distances and bond angles.

Both crystal structures are built up from one crystallographically independent 4-substituted thiophene ring. In both cases, the molecules have a centre of symmetry at the midpoint of the C(2)–C(2′) bond, and hence the coplanarity between the individual ring and the *anti* orientation of the sulfur ring atoms with respect to the inter-ring bond are crystallographically dictated. It is of interest to note that the same, crystallographically imposed, *anti* coplanar conformation was previously observed in most of the 2,2′-dithienyls of known structure, namely the 2,2′-bithiophene,[8] and its 5,5′-dibromo[9] and 3,3′-dimethoxy[10] substituted derivatives.

Bond distances and bond angles in compound I*tt*, although of low accuracy (see the Experimental section), are in the expected ranges,[11] and compare well with those previously reported for other dithienyl derivatives.[8–10] The thiophene ring is planar within the experimental uncertainties, the maximum atomic deviation from the mean least-square plane being 0.003 Å. The planar molecules are stacked in parallel layers along the shortest cell axis (*a*) and none of the intermolecular contacts is less than 3.60 Å. It is noteworthy that this also occurs in the bithiophene derivatives of known structure.[8–10] The shortest intermolecular S ··· S separation in compound I*tt* is 4.104(2) Å.

Bond distances and angles in compound II*tt* do not differ significantly from the corresponding values of compound I*tt*, and agree well with those determined by electron diffraction on gaseous bithiophene.[4] These values and the extra-ring C–S

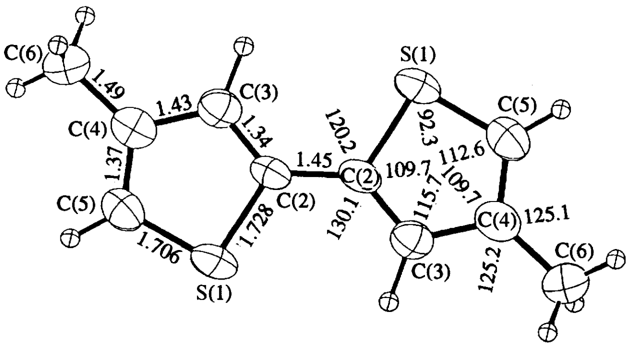


Fig. 1 ORTEP[7] plot of compound I*tt* with atom numbering scheme, bond distances (Å, esds for C–S bonds ±0.006–0.008, C–C bonds ±0.01), bond angles (deg, esds ±0.4–0.8). Thermal ellipsoids for non-H atoms enclose 40% probability. Equivalent atoms are related by an inversion centre at the midpoint of the C(2)–C(2) bond.

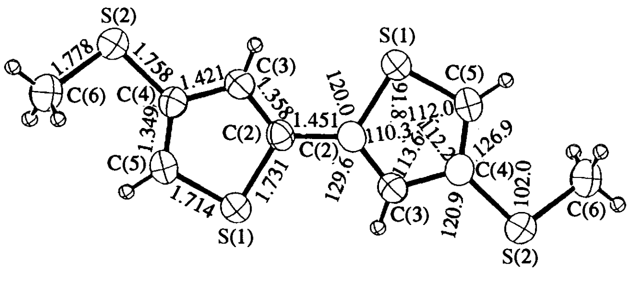


Fig. 2 Atom numbering scheme, thermal ellipsoids (40%), bond distances (Å, esds for C–S bonds ±0.002–0.003, C–C bonds ±0.003–0.004) and bond angles (deg, esds ±0.1–0.3) for compound II*tt*. Equivalent atoms are related by an inversion centre at the midpoint of the C(2)–C(2) bond.

bond distances indicate that the electronic properties of the S–CH_3 substituent do not affect the conjugation between thiophene rings. The latter are planar within ±0.008 Å. Only the methyl carbons are significantly displaced (0.535 Å) from the mean molecular plane, and their orientation may be described in terms of a C(5)–C(4)–S(2)–C(6) torsion angle of 17.7(3)°.

As for compound I*tt*, the molecular packing of II*tt* does not contain interatomic distances less than 3.60 Å. Nevertheless, a relatively short [3.878(1) Å] S···S separation between the sulfur ring atom and that of the substituent was found to be present.

MM2 calculations of the conformation of compounds II*hh*, II*ht* and II*tt*

MM2 calculations on compounds II*hh*, II*ht* and II*tt* were carried out by adding the parameters for CH_2=CH–S–CH_3[12] to Allinger's program MM2(91), parametrized for thiophene.[13] The results are reported in Table 1, together with the values of the maximum UV absorption. For comparison, the λ_{max} values for compounds I are given in parentheses.

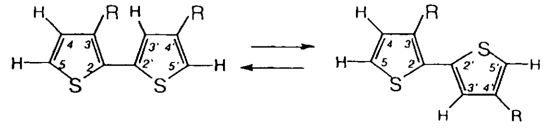
The trend of variation of the conformation of compounds II with the regiochemistry of substitution and the relative permittivity of the medium is similar to that found for the dimethyl derivatives I.[6c] Thus, the change of relative permittivity from 1.5 to 5.0 (a value close to the relative permittivity of chloroform) has a marked stabilizing effect on the *syn* forms, an effect which in II*tt* leads to the reversal of the conformational preference from the *anti* to the *syn* form. For II*hh*, the energy difference between the *anti* and the *syn* conformation is so large that the *anti* conformation predominates regardless of the value of the relative permittivity. It is worth noting that the *syn* forms of compounds II*ht* and II*tt* are almost planar according to MM2 calculations, while the *anti* forms are highly twisted.

For compounds II, the question arises as to the orientation of the methyl group of the SCH_3 fragment with respect to the aromatic ring. According to electric dipole moment measurements in benzene and semi-empirical calculations, in 3-(methylsulfanyl)thiophene there is an equilibrium between planar *syn*-like and gauche *anti*-like orientations.[14]

According to our MM2 calculations, the SCH_3 group in bithiophenes II is quasi orthogonal to the ring plane regardless of the relative permittivity of the medium. Moreover, the orientation of SCH_3 has only a minor effect in the preferred conformation of the aromatic skeleton.

^{1}H NMR (NOE) of compounds I*ht*, II*ht* and II*tt*

The head-to-tail compounds I*ht* and II*ht* have no elements of symmetry except the mean molecular plane. In principle, some information on the conformational preferences of these compounds could be obtained by irradiating the methyl groups and observing the nuclear Overhauser effects[15] on the aromatic protons. In particular, if there is an equilibrium between the *syn* and *anti* conformations in solution, such as that reported in Scheme 2 and predicted by MM2 calculations, a positive NOE should be measured for 3′-H upon irradiation of the methyl group at C-3. In the *anti* conformation, the distance between the substituent at C-3 and the H-3′ proton would be too large to observe any nuclear Overhauser effect.



Scheme 2 *Syn* ⇌ *anti* conformational equilibrium of I*ht* (R = CH_3) and II*ht* (R = SCH_3)

Moreover, the NOE measured between the 4′-SCH_3 group and the adjacent 3′-H and 5′-H in the head-to-tail derivative II*ht*, as well as the NOE measured between 4-SCH_3, 4′-SCH_3 groups and the adjacent 3-H, 3′-H and 5-H, 5′-H protons in the tail-to-tail derivative II*tt*, can give information on the preferred orientation of the methylsulfanyl group.

Table 2 gives the NOE values measured for the aromatic protons of I*ht*, II*ht* and II*tt* in chloroform following irradiation of the CH_3 and SCH_3 groups.

It can be seen that irradiation of 4′-SCH_3 in II*ht* gives similar NOE effects on 3′-H and 5′-H, 16% and 13%, respectively. This result is in agreement with MM2 calculations, which predict an orientation of the methylsulfanyl group orthogonal to the ring plane. As far as compound II*tt* is concerned, the data in Table 2 show that there is a 10% and 15% NOE on 3-H, 3′-H and 5-H, 5′-H, respectively, upon irradiation of the 4-SCH_3, 4′-SCH_3 groups. The observation of a substantial NOE effect on 3-H, 3′-H rules out the possibility that the SCH_3 group is in the same *syn*-like conformation observed in the solid, and is also in agreement with MM2 calculations.

The data in Table 2 also show that there is a positive NOE between the 3-CH_3 or 3-SCH_3 groups and 3′-H belonging to the adjacent ring, 21% and 3% NOE for I*ht* and II*ht*, respectively. This result unambiguously indicates the presence of non-negligible amounts of *syn* conformations for both compounds in solution. Attempting to quantify this presence in terms of percentage of *syn* conformations is hazardous, since the NOE effect depends on the sixth power of the distance between the interacting protons[15] and with the aid of molecular models it can easily be seen that even small variations of the inter-ring twist angles lead to large variations in these distances.

Table 1 MMP2 calculated inter-ring twist angles ($\omega/°$), conformational energies (E/kJ mol^{-1}), relative populations (p/%) and maximum UV absorption (λ_{max}/nm) of compounds **II***hh*, **II***ht* and **II***tt* for two different values of the relative permittivity (1.5 and 5.0)

Compound	ω^b	$E_{1.5}$	$p_{1.5}{}^b$	E_5	$p_{5.0}{}^b$	$\lambda_{max}{}^c$
II*hh*	±40	140.65	0	121.81	0	279 (268)
	±127	112.82	100	99.28	100	
II*ht*	±2	108.68	11	90.04	65	331 (299)
	±136	103.41	89	91.58	35	
II*tt*	0	93.51	17	75.16	83	327 (311)
	±149	91.37	83	80.76	17	

[a] ω is the dihedral angle 1–2–2′–1′. A dihedral angle of 0 ° corresponds to a *syn* planar conformation. We believe this definition of the dihedral angle is more convenient than that of ref. 6(*c*) since it is more generally used. [b] The relative populations were calculated taking into account the entropy factor. [c] Taken from ref. 16. The values in parentheses are those for the corresponding isomers of compounds **I**.[6c]

Table 2 NOE effects (in CDCl$_3$) of compounds **I***ht*, **II***ht* and **II***tt*

Compound	Irradiated nucleus	Observed nucleus	NOE (%)
I*ht*	3-CH$_3$	4-H	28
		3′-H	21
I*ht*	4′-CH$_3$	3′-H	22
		5′-H	19
II*ht*	3-SCH$_3$	4-H	18
		3′-H	3
II*ht*	4′-SCH$_3$	3′-H	16
		5′-H	13
II*tt*	4-SCH$_3$, 4′-SCH$_3$	3-H, 3′-H	10
		5-H, 5′-H	15

Discussion

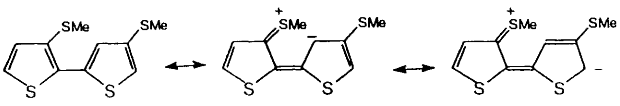
Figs. 1 and 2 show that the solid state structures of **I***tt* and **II***tt* display large dissymmetries of the thiophene rings. In particular, both compounds have the inner S1–C2 bond significantly longer than the external S1–C5 bond. This is a manifestation of what is called the 'plasticity' of oligo- and poly-thiophenes, namely of the capability of these substrates to minimize the conformational strain, due to intra- and inter-molecular interactions, by deforming the thiophene rings through a series of successive and cooperative elongations of the C–S and C–C bonds and adjustments of the bond angles.[2a,h] This property, originating from the great polarizability of the sulfur atom, allows for the existence of unexpected solid state conformations, such as, for example, the conformation of a head-to-head tetramethylquaterthiophene in which the methyl substituents are in the *syn* orientation.[2h] Very likely, the deformations observed in **I***tt* and **II***tt* are due to the need to relieve the severe S···CH interactions present in the *anti* coplanar conformation. In this respect, it is significant that deformations of the same type are found even in the non-planar *anti* conformation of bithiophene in the gaseous state, in which the inner C–S bond is 0.014 Å longer than the outer one.[4a]

The need for a better definition of the ambiguous conformational properties of oligo- and poly-thiophenes has prompted several theoretical investigations of the energy profiles of 2,2′-bithiophene and its dimethyl derivatives, carried out at various levels of sophistication.[5] For 2,2′-bithiophene semiempirical AM1,[5b] *ab initio* 6-31G*[5a] and 6-31G**[5a] calculations indicate the existence of two energy minima, corresponding to the *syn*-like (ω = 30–40°) and to the *anti*-like conformations (ω = 150°). The calculations are in agreement with the results of electron diffraction data.[4] For 3,3′- and 3,4′-dimethyl-2,2′-bithiophenes semiempirical[5b] and *ab initio* 3-21G*[5a,c] and 6-31G*[5a,c] calculations indicate the existence of one single minimum with ω around 90–100°. Since **I***ht* and **I***hh* display different λ_{max} values in chloroform, thus indicating a very different degree of π–π conjugation for the two compounds, it is unlikely that the perpendicular or quasi perpendicular conformation predicted by these calculations is the one predominating in solution. No electron diffraction data are currently available to verify whether this is the conformation predominating in the gas phase.

Searching for a method capable of giving us some information on the conformational properties of substituted bithiophenes and longer oligothiophenes without requiring long computer times or sophisticated computer resources, we carried out non-quanto mechanical force field MM2 calculations of the conformation of bi- to sexi-thiophenes using Allinger's MM2(91) program parametrized for thiophene.[13] One advantage of this type of calculation is that it can give the trend of solvent effects on conformation. MM2 calculations on unsubstituted 2,2′-bithiophene indicate the existence of two energy minima corresponding to the *syn* coplanar and to the *anti* twisted conformation, the latter being preferred by 1.12 kJ mol^{-1}. The comparison of these results with the electron diffraction data[4a] indicates that MM2 calculations over emphasize the tendency towards the planarity of the *syn* conformation. However, even the most sophisticated *ab initio* calculations on 2,2′-bithiophene reproduce the geometry of the *anti* conformation better than that of the *syn*, probably due to the fact that the non-bonded S···S interactions are not sufficiently well described. Contrary to semiempirical and *ab initio* calculations of 3,4′- and 3,3′-dimethyl-2,2′-bithiophenes, MM2 calculations on the same compounds predict the existence of two energy minima and a greater degree of twisting for **I***hh* than for **I***ht*, in agreement with the λ_{max} values.[6a,c] Even more importantly, MM2 calculations predict the existence of *syn* $\rightleftharpoons$ *anti* conformational equilibria for **I***ht* and **II***ht*, *cf.* Table 1 and ref. 6(*a*, *c*). These predictions can be checked by carrying out NOE measurements in solution of these derivatives. In fact, if *syn* conformations are present in solution, a positive NOE effect between the methyl group at C-3 and 3′-H on the adjacent ring should be observed (*cf.* Scheme 2). The NOE data reported in Table 2 show that there is, in fact, a substantial presence of *syn* conformers for **I***ht* as well as for **II***ht*, indicating that the MM2 predictions are correct. Thus, it can be concluded that MM2 calculations give a reasonably good, although qualitative, representation of the conformational properties of oligothiophenes to use as a guideline in the interpretation of experimental results.

According to MM2 calculations, **I***tt* and **II***tt* should also exist in chloroform as equilibria of *syn* and *anti* conformers. For **I***tt* this is in agreement with the conclusions reached on the basis of ^{13}C NMR chemical shift arguments.[6a] Since **I***tt* and **II***tt* are symmetric molecules, direct evidence of the presence of *syn* conformers by NOE measurements cannot be obtained. However, the fact that a sizeable amount of *syn* conformations is present in chloroform for **I***ht* and **II***ht* is strong indirect evidence in this direction, since the steric interactions in the *syn* conformation of tail-to-tail isomers should be smaller than in their head-to-tail counterparts. On the other hand, if there is a *syn* $\rightleftharpoons$ *anti* equilibrium of I*tt* and II*tt* in chloroform, then the conformational preferences of both compounds in solution are different from those in the solid. An indication that this is the case for II*tt* comes from the NOE data reported in Table 2, indicating that the SCH_3 group in solution is in the quasi perpendicular orientation, while in the solid it is in the *syn*-like orientation. The existence of conformational differences between the solid and the liquid state have already been pointed out in the case of longer oligothiophenes.[2g–i]

A final comment concerns the observation that the trend of variation of the λ_{max} values (*cf.* Table 1) with the regiochemistry is not the same for compounds I and II, despite the fact that, according to MM2 calculations, these compounds have very similar geometries and conformations. For substrates I, the experimental λ_{max} values in chloroform are in the order I*tt* > I*ht* > I*hh* and reflect the degree of planarity of these compounds. In fact, as the degree of planarity increases on going from the head-to-head to the tail-to-tail derivative, the π-π electron delocalization increases and the λ_{max} value increases. For compounds II, the λ_{max} values are in the order II*ht* > II*tt* > II*hh*, *i.e.* the λ_{max} for the head-to-tail derivative is greater than that for the tail-to-tail one. The reason for this apparent contradiction is in the mesomeric effect exerted by the methylsulfanyl substituents in derivatives II. In II*ht* and II*hh*—but not in II*tt*—the lone pair of the SCH_3 groups at C-3 and C-3′ can be delocalized not only onto the ring to which it is bound but also onto the adjacent ring, as illustrated for compound II*ht* (*cf.* Scheme 3).



Scheme 3

Thus, the λ_{max} value of compounds II reflects not only the degree of planarity of the system but also the delocalization capability of the lone pairs of the substituents, which depends, in turn, on the regiochemistry of substitution. In the case of compound II*ht*, only the sulfur atom at C-3 can delocalize its lone pair on the adjacent ring while in compound II*hh* this is possible for the lone pairs of both substituents. To have an idea of the importance of the dependence of the mesomeric effect on the regiochemistry of substitution, we calculated the λ_{max} value of compounds II*tt*, II*ht* and II*hh* with the aid of the CNDO/S program,[17] imposing on the three dimers the *anti* planar conformation. The values obtained in this way were: 338 nm for II*hh*, 333 nm for II*ht* and 326 nm for II*tt*, indicating that in coplanar conformations the inter-ring mesomeric effect of SCH_3 is, in fact, the greatest for the 3,3′-disubstituted regioisomer. It is worth noting that the calculated λ_{max} values for II*ht* and II*tt* in the *anti* planar conformation are rather close to the experimental ones, indicating that these compounds are characterized by a high degree of planarity in chloroform. For the twisted II*hh* compound, the real importance of the mesomeric effect exerted by the methylsulfanyl groups will depend on the value of the inter-ring twist angle, since the tendency to maximize the electron delocalization through a planar conformation will be counteracted by the steric interactions among substituents. Since the λ_{max} value calculated for the planar *anti* conformation of II*hh* is much larger than the experimental value, it must be inferred that II*hh* exists in chloroform in a largely twisted conformation. CNDO/S calculations of the λ_{max} value for this compound using the geometry derived from MM2 calculations and varying the inter-ring twist angle ω showed that the experimental value of 279 nm should correspond to an ω of roughly 110°. Thus, despite its greater λ_{max} value, II*hh* in chloroform is more twisted than its dimethylated counterpart I*hh*. In other words, the methylsulfanyl group has a greater 'defect' effect than the methyl group.

Conclusions

We have shown that, despite the great differences in the electronic and steric properties of the methyl and methylsulfanyl substituents, the conformational trends of the head-to-head, head-to-tail and tail-to-tail regioisomers of dimethyl- and bis(methylsulfanyl)-2,2′-bithiophenes are very similar and appear to be more related to the regiochemistry of substitution than to the intrinsic properties of the substituents.

Our data confirm that oligothiophenes are highly deformable compounds, characterized by great conformational variability. Finally, the present paper reports the first unambiguous experimental evidence of the existence of *syn* conformations in solutions, a result which might help to elucidate the origin of the solvatochromic properties of oligo and polythiophenes.[18]

Experimental

Substrates

Compounds I and II were synthesized according to the procedures reported in refs. 6(*c*) and 16, respectively.

Crystal data and X-ray structure analysis.

Single crystals of compounds I*tt* and II*tt* were grown by slow evaporation of cyclohexane solutions. Intensity data were collected at room temperature using graphite monochromated Mo-Kα radiation and the ω-2θ scan mode.

Compound I*tt*: $C_{10}H_{10}S_2$, $M = 194.31$. Monoclinic, $a = 5.822(2)$, $b = 7.353(2)$, $c = 11.355(4)$ Å, $V = 482.8(9)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections ($\lambda = 0.7107$ Å), space group $P2_1/n$ (n° 14), $Z = 2$, $D_x = 1.336$ g cm^{-3}, $F(000) = 204$. Colourless prisms, crystal dimensions 0.30 × 0.25 × 0.25 mm, μ(Mo-Kα) = 4.35 cm^{-1}.

Compound I*tt* sublimed rather quickly, hence the selected crystal was sealed into a glass capillary. Intensity data were collected on a CAD4 diffractometer. ω Scan width was $(1.50 + 0.35 \tan \theta)°$, ω scan speed 1.18–2.06° min^{-1}. Of 896 measured reflections ($2 \leq \theta \leq 26°$) 488 had $I \geq 2\sigma(I)$ and 445 were unique ($R_{int} = 0.014$) and were used, without absorption correction which was deemed unnecessary, in the structure analysis. The intensities of two standard reflections monitored at 1 h intervals showed no significant changes. Although of poor quality, due to a high mosaic spread of the crystals, the intensity data obtained proved sufficient to allow for a satisfactory determination of the molecular dimensions.

The structure of compound I*tt* was solved by direct methods (SHELX 86),[19] and refined through full-matrix least-squares calculations (SHELX 76).[20] Non-H atoms were refined anisotropically; H atoms, located in ΔF maps, were refined isotropically through some least-squares cycles and then held fixed because of the low reflection/parameter ratio. The weighting scheme $W = 0.78/[\sigma^2(F_o) + 0.009\,04\ F_o^{\,2}]$ gave satisfactory agreement analyses. Final R and R_w values were 0.076 and 0.077.

Compound II*tt*. $C_{10}H_{10}S_4$, $M = 258.45$. Monoclinic, $a = 7.786(1)$, $b = 9.190(1)$, $c = 8.815(1)$ Å, $\beta = 110.88(1)°$, $V = 589.3(1)$ Å^3 (by least-squares refinement on diffractometer angles for 36 automatically centred reflections ($\lambda = 0.7107$ Å), space group $P2_1/c$ (n° 14), $Z = 2$, $D_x = 1.456$ g cm^{-3}, $F(000) = 268$. Colourless, air stable prisms. Crystal dimensions 0.32 × 0.18 × 0.18 mm, μ (Mo-Kα) = 6.92 cm^{-1}.

Intensity data were collected on a Siemens P4RA-M18X diffractometer (40 kV, 70 mA). Scan width was $2\theta(K\alpha_1) -0.6$ to $2\theta(K\alpha_2) +0.6$, scan speed 4–30° min^{-1}. Of 2162 measured reflections ($2 \le \theta \le 29°$) 1258 had $I \ge 3\sigma(I)$ and 926 were unique ($R_{\text{int}} = 0.024$). An empirical absorption correction based on the ψ scan[19] was applied to intensities ($0.603 \le$ transmission ≤ 0.629).

The structure of compound **II***tt* was solved by direct methods (SHELX 86)[20] and refined through full-matrix least-squares calculations (SHELX 76).[21] Non-H atoms were treated anisotropically and H atoms, located in ΔF maps, isotropically (with common B for those bonded to the same atom). The weighting scheme $W = 1.034/[\sigma^2(F_o) + 0.000\,556\,F_o^2]$ gave satisfactory agreement analyses. Final R and R_w values were 0.034 and 0.039.

Scattering factors were from SHELX 76.[21] Most of the calculations were carried out on a VAX 6310 computer. Tables of final fractional coordinates and full lists of bond distances and bond angles of compounds **I***tt* and **II***tt* have been deposited at the Cambridge Crystallographic Data Centre.†

Theoretical calculations

All calculations were carried out with a Vax Station 2000 using MM2(91) and CNDO/S programmes (13, 17).

NMR spectroscopy

^{1}H NOE data were obtained with a Bruker AMX-400 WB spectrometer operating at 400.13 MHz. The CDCl$_3$ solutions were accurately degassed by means of five freeze–pump–thaw cycles. Differential steady-state NOE experiments were performed acquiring 128 + 128 transients in groups of 8, alternately irradiating on and off-resonance, with a presaturation time of 10 s. Decoupler attenuation was set for maximum selectivity.

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