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1,2-Dithiins and Precursors, XVII[1]: Synthesis and Properties of Thieno Anellated 1,2-Dithiins, Structural Influence on Colour

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Abstract: Various thieno[3,2-*c*] anellated (**5a**, **26**) and dithieno[3,2-*c*:2,3-*e*] anellated 1,2-dithiins (**32 a-c**, **45**) were obtained starting from appropriate thiophene precursors. The absorption maxima covered the range from 430 to 467 nm indicating olefinic rather than aromatic character of the anellating thiophene units. Access to the isomeric thieno[2,3-*c*] anellated series failed due to competing reactions in the final stage, e.g. by the formation of the 12-membered cyclic bis-disulfide **53**.

Introduction

One of the outstanding properties of 1,2-dithiin (**1**) is its red colour which, even today, presents a theoretical challenge with respect to the non-planar ring structure and the absence of any classical chromophore (*Scheme 1*).[2]

As previously noted, the wavelength of the absorption maximum in the visible region depends significantly on substitution (especially in positions 3 and 6) as well as on anellation.

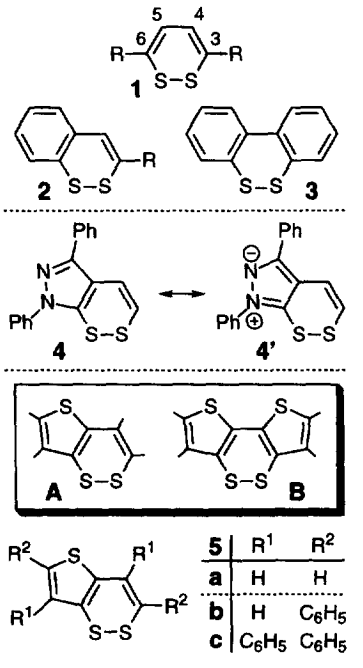
Unsaturated, aromatic, and heteroaromatic substituents produce bathochromic shifts of the absorption maximum from 457 nm in the parent compound **1**, R = H,[1,3] up to about 500 nm, possibly due to an extension of the butadiene conjugation.[4] Accordingly the bathochromic shift of 3,6-di(α-thienyl)-1,2-dithiin (**1**, R = α-thienyl: λ_{max} = 478 nm) compared to 3,6-diphenyl-1,2-dithiin (**1**, R = C_6H_5: λ_{max} = 467 nm)[1,3] could be interpreted by the increased double bond character of thiophene relative to benzene.

On the other hand, aromatic anellation gives rise to a pronounced hypsochromic shift of the absorption maximum in the visible region as shown by 1,2-benzodithiin (**2**, R = H) with λ_{max} = 407 nm,[4c] and by the colourless dibenzo[*c*,*e*][1,2]dithiin (**3**)[5]. In addition, pyrazolo-1,2-dithiin **4/4'** with λ_{max} = 406 nm has a hypsochromically shifted long wave absorption.[6] In these cases the π-electron pairs of **1** are rather delocalized within the anellating π-system and less availble for the 8π-electron arrangement of the 1,2-dithiin ring.

Hence the question arises: To what extent the light absorption of a 1,2-dithiin may be used as an „indicator" in order to ascertain the degree of delocalization or aromaticity of any anellated π-system?

With regard to this question, thieno[3,2-*c*] anellated 1,2-dithiins of type **A** as well as the corresponding dianellated species **B** were considered to be especially informative molecules with respect to the extreme hypsochromic effects caused by benzo anellation.[7]

The early investigations of *Behringer* and *Meinetsberger* 15 years ago[8] produced the surprising result that **5b** and **5c**, analogues of **A**, show „normal" absorptions in the visible region [λ_{max} = 467 nm (**5b**) and λ_{max} = 455 nm (**5c**)]. Thus, further investigations in this series, including the parent compound **5a** as well as other representatives of **A** and **B**, appeared to be of significant interest regarding colour, and we report now the results of our study.



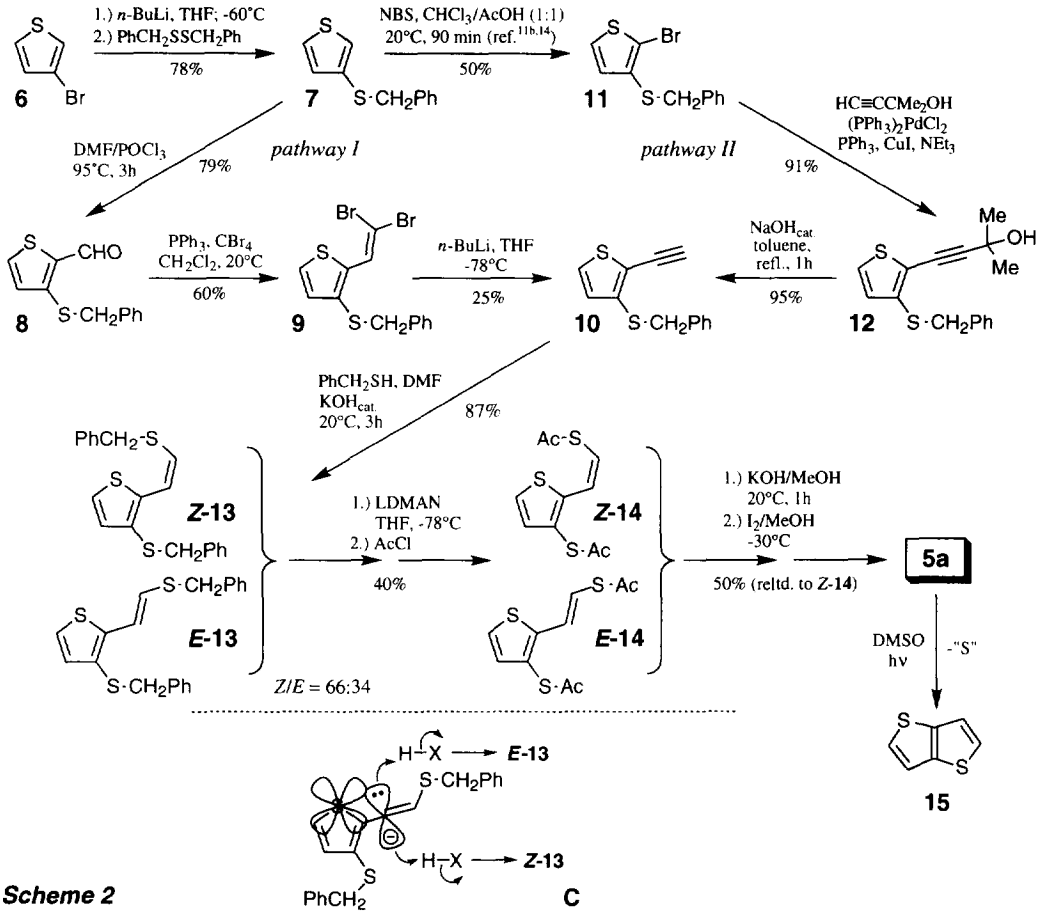
Scheme 1

It should be emphasized however, that the formation of **5b,c** was the result of an unusual „witches brew",[9] which proved to be unsuitable for a general entry into the series. Therefore, our strategy was largely based on a systematic assembly of the cyclic disulfide ring starting from appropriate thiophene precursors.

Results and Discussion

1. Thieno[3,2-*c*][1,2]dithiin (5a;

The synthesis of **5a** could be accomplished starting from bromothiophene **6** via bromo-lithium exchange with *n*-BuLi at low temperature[10] and subsequent thiolation with dibenzyldisulfide in a one-pot reaction yielding benzylthiothiophene **7** (*Scheme 2*).[11,12] Two alternative pathways via 3-benzylthio-2-ethynylthiophene (**10**) as the key intermediate were possible.



Scheme 2

As first step in *pathway I* (C_2+C_1+C_1 assembly) a formyl group was introduced into **7** by Vilsmeier reaction to yield **8**. The selective substitution in 2-position is unambiguously proved by the doublets of the two thiophene protons. Subsequent Corey-Fuchs ethynylation via dibromovinyl intermediate **9** furnished the ethynylthiophene **10**.[13] Debromination of **9** could only be carried out, however, with greater loss.

Generally better yields were obtained in *pathway II* (C_2+C_2 assembly). This sequence begins with NBS bromination of **7** smoothly producing the 2-bromo derivative **11**.[11b,14] The latter mediated the direct introduction of an acetylene unit by Pd-catalyzed bromo exchange with 2-methyl-3-butyn-2-ol to afford **12**. In this reaction an optimal ratio of the Pd catalyst to PPh_3 is of decisive importance.[15] Final deprotection of the latter with catalytic amounts of sodium hydroxide in boiling toluene again gave **10**.

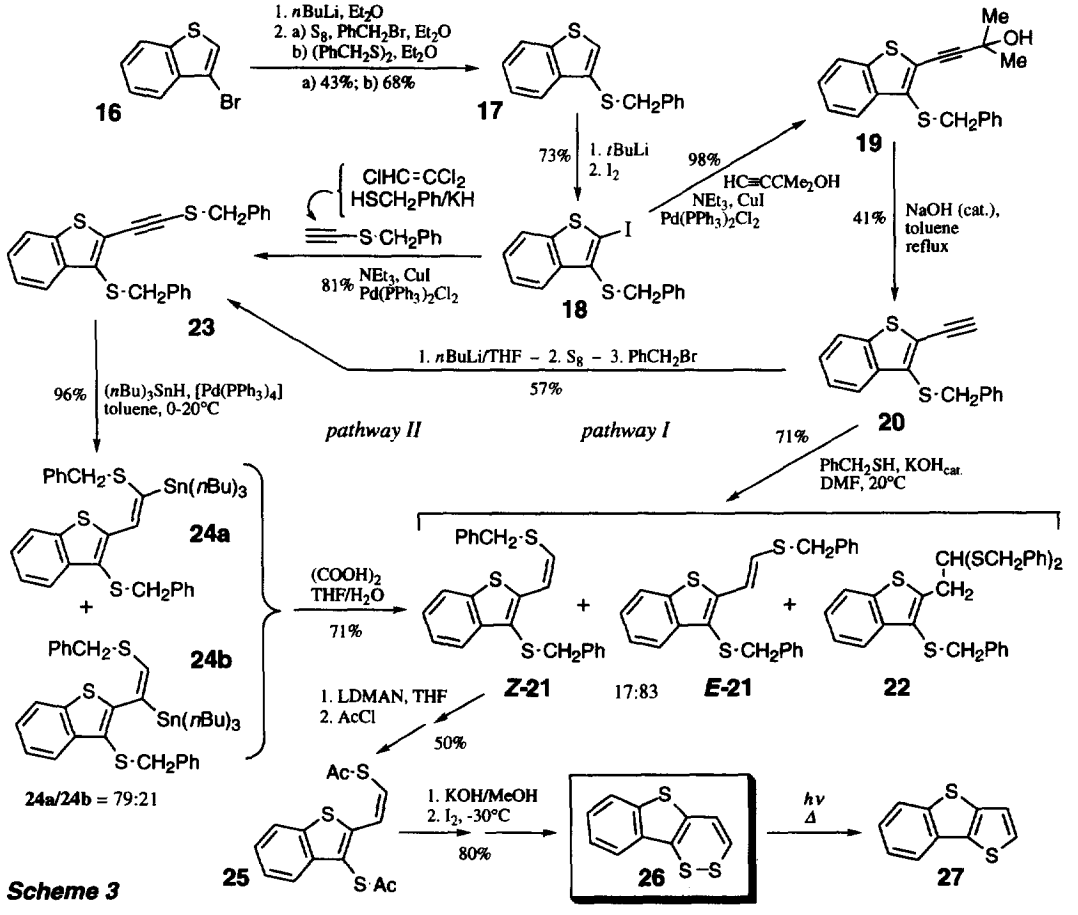
The latter should permit nucleophilic addition of benzylmercaptan leading exclusively to addition product *Z*-**13** as demonstrated by our approach to non-anellated 1,2-dithiins.[1,3] In contrast to this however, KOH catalyzed addition of phenylmethanethiol in DMF furnished a 66:34 *Z*/*E*-mixture of 3-benzylthio-2-(2-benzylthiovinyl)thiophenes **13**, indicated by two sets of olefinic proton signals in the NMR spectrum with coupling constants J = 10.65 Hz for the *Z*- and J = 15.47 Hz for the *E*-isomer. In situ debenzylation of **13** with the aid of

lithium 1-dimethylaminonaphthalenide[16] and subsequent reaction with acetyl chloride produced the *Z/E*-isomeric 3-acetylthio-2-(2-acetylthiovinyl)thiophenes **14**, isolated as easily stored crystalline equivalents of the correspondent 1,4-dithiolates. Regeneration of the latter by saponification with methanolic KOH and oxidation with I_2 finally furnished **5a** which, after column chromatography, was obtained as dark red oil in 50% yield (related to *Z*-**14**).

The surprising failure of stereoselectivity in the transformation of **10** to **13** may be caused by a briefly existing carbanion intermediate which is, according to **C**, stabilized by interaction of the exocyclic α-C p_z-orbital with the sulfur d-orbital of thiophene allowing subsequent protonation at both sites.[17a]

The absorption of thieno[3,2-*c*][1,2]dithiin (**5a**) at λ_{max} = 441 nm is more shortwave-shifted compared with that of the phenyl substituted analogues **5b,c**, however much more bathochromicly shifted relative to 1,2-benzodithiin (**2**) (for values see above). Furthermore, **5a** in solution undergoes sulfur extrusion in daylight more readily than the benzo analogue **2** forming thieno[3,2-*b*]thiophene (**15**) with decolourization. Consequently the preliminarily measured quantum yield in EtOH was Φ = 0.47 (at λ_{irr} = 436)[17b] whereas with that of **2**, R = CH_3,[4c] was only Φ = 0.20 (at λ_{irr} = 405 nm).

2. Benzo[4,5]thieno[3,2-*c*][1,2]dithiin (26)



Scheme 3

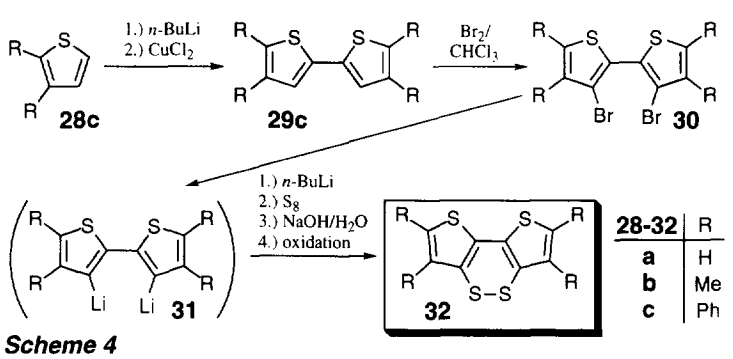
Two routes for the access to **26** were attempted, in each case based on a C_2+C_2 assembly via 3-benzylthio-2-iodobenzo[b]thiophene (**18**) as key intermediate (*Scheme 3*). The introductory sequence parallels that of the synthesis of **5a** (see *Scheme 2*) and proceeds via transformation of 3-bromobenzo[*b*]thiophene (**16**) to 3-benzylthiobenzo[*b*]thiophene (**17**) and conversion of the latter to **18**.

In *pathway I* a Pd^0-mediated reaction of **18** with 2-methyl-3-butyn-2-ol afforded almost quantitatively the ethynyl derivative **19**, from which 3-benzylthio-2-ethynylbenzo[*b*]thiophene (**20**) could be liberated. Subsequent nucleophilic addition of benzylmercaptan to the triple bond again afforded a (*Z*/*E*)-mixture of the benzylthiovinyl products **21**, as already noted in the synthesis of **5a** (cf. *Scheme 2, pathway II*) and explained by **C**. However, a much more disadvantagous (*Z*/*E*)-ratio of 17:83 was obtained. In addition, the corresponding mercaptal **22** was formed in a further addition reaction.

Exclusive access to the (*Z*)-isomer of **21** could be achieved by *pathway II* following the *Block* methodology[4b] via benzylthioethynylbenzothiophene **23** as the key intermediate which was obtained from either **18** or from **20**. In the first case, **23** arose from a C,C-coupling of **18** with benzylthioacetylene (advantageously accessible by base assisted reaction of trichloroethylene with phenylmethanethiol by analogy with ref.[18]). In the latter case, the ethynyl group was successively functionalized by deprotonation, sulfurization and benzylation. Addition of tributylstannyl hydride to **23** smoothly afforded a mixture of the regio-isomeric stannyl products **24a,b** from which the stannyl group could be easily removed by hydrolysis to give *Z*-**21**. The subsequent course parallels again that described in *Scheme 2*, namely reductive debenzylation by means of LDMAN and in-situ acetylation of the resulting dithiolate to yield the diacetylthio derivative **25**. Regeneration of the dithiolate and in-situ oxidation furnished the benzothieno-1,2-dithiin **26** in brick-red leaflets.

This 1,2-dithiin derivative shows an absorption at λ_{max} = 459 nm, which is 18 nm bathochromicly shifted compared with **5a** and is obviously due to the more olefinic character of the anellated thiophene unit. The action of daylight to a solution of **26** resulted in sulfur extrusion forming the colourless benzothienothiophene **27** as well as undefined byproducts.

3. Dithieno[3,2-c:2',3'-*e*][1,2]dithiins (32)



Scheme 4

The synthesis proved to be relatively uncomplicated via disulfane bridging within a suitable 2,2'-dithienyl derivative (*Scheme 4*).[19] Common intermediates were the 3,3'-dibromo-2,2'-dithienyls **30**. Both **30a,b** had already been described in literature,[20] and **30c** was easily prepared by lithiation and subsequent oxidative C,C coupling of 2,3-diphenylthiophene (**28c**) and bromination of the resulting coupling product **29c**. The incorporation of the disulfane bridge to produce **32** was smoothly accomplished by in situ bromo-lithium exchange via **31** and reaction with elemental sulfur. The yield of the transformation from **30** to **32a** (19%) was essentially lower than that to the substituted dithiins **32b** (64%) and **32c** (61%), obviously due to competing lithiation at other thiophene positions.

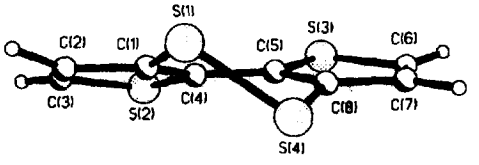
The dithieno anellated 1,2-dithiins **32** form red crystals with long wave absorption maximum at 430 nm for **32a**, 441 nm for **32b**, and 450 nm for **32c**. Thus, also in this series no marked similarity with the colourless dibenzo[*c*,*e*][1,2]dithiin (**3**)[5] can be recognized. An electrocyclic ring-opening of **32** to a thioxo valence isomer, which represents a thioxoindigoid system, is unambiguously excluded by the failure of any ^{13}C NMR indication of the C=S group.

According to the X-ray analysis of **32a** [21] the disulfide ring is clearly twisted. As illustrated in *Fig. 1*, the C-S-S-C dihedral angle of about 51° characterizes a compromise between a dihedral angle of 0° in the planar state with a maximum strained disulfide unit and 90° in the strain-less state of this unit. Avoidance of „antiaromaticity" in the case of a planar 8π-electron system may also be of consideration. The two thiophene planes are distorted about 20° to each other.

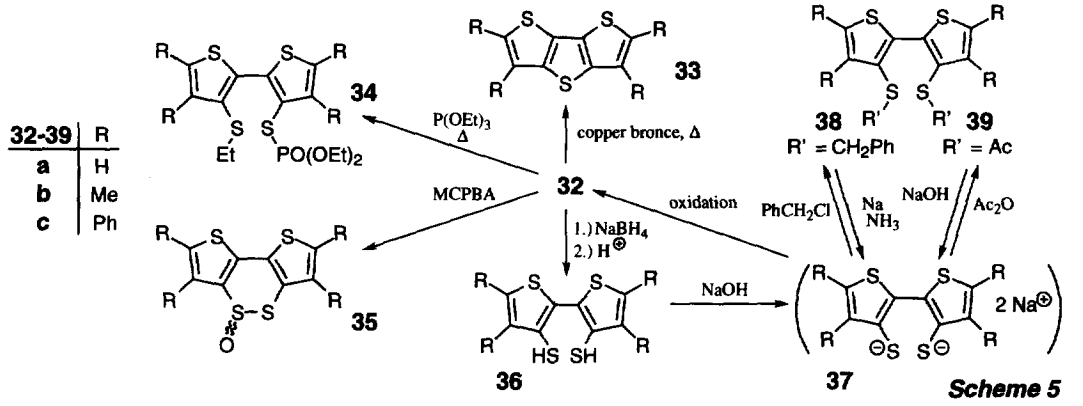
In contrast to non- and mono-anellated 1,2-dithiins but in accord with other di-anellated species, the compounds **32** are resistant to a daylight induced sulfur extrusion (*Scheme 5*). This reaction could be performed

only by means of copper bronze at elevated temperature to yield the dithienothiophenes **33**. An attempt to extrude sulfur from **32** with triethyl phosphite as a typical thiophilic agent produced the thiophosphoric esters **34** clearly via S,S-bond heterolysis by P-attack and successive S-alkylation.

Figure 1.



X-ray crystal structure of dithieno[3,2-c:2',3'-e][1,2]dithiin (**32a**).[21] The asymmetric unit cell contains two molecules. – Important bond lengths [Å] and angles [°]: S(1)-S(4) 2.059(3), S(1)-C(1) 1.768(6), S(4)-C(8) 1.723(6), C(1)-C(4) 1.363(9), C(5)-C(8) 1.373(9), C(4)-C(5) 1.419(10); S(1)-C(1)-C(4) 121.62(40), C(1)-C(4)-C(5) 126.13(50), C(4)-C(5)-C(8) 125.12 (52), C(5)-C(8)-S(4) 121.34 (42), C(8)-S(4)-S(1) 99.37(27), S(4)-S(1)-C(1) 99.57(25); C(1)-S(1)-S(4)-C(8) 50.85(29), S(1)-S(4)-C(8)-C(5) -42.03(53), C(4)-C(5)-C(8)-S(4) 7.09(71), C(1)-C(4)-C(5)-C(8) 19.90(85), S(1)-C(1)-C(4)-C(5) 4.03(80), S(4)-S(1)-C(1)-C(4) -39.64(51).



Scheme 5

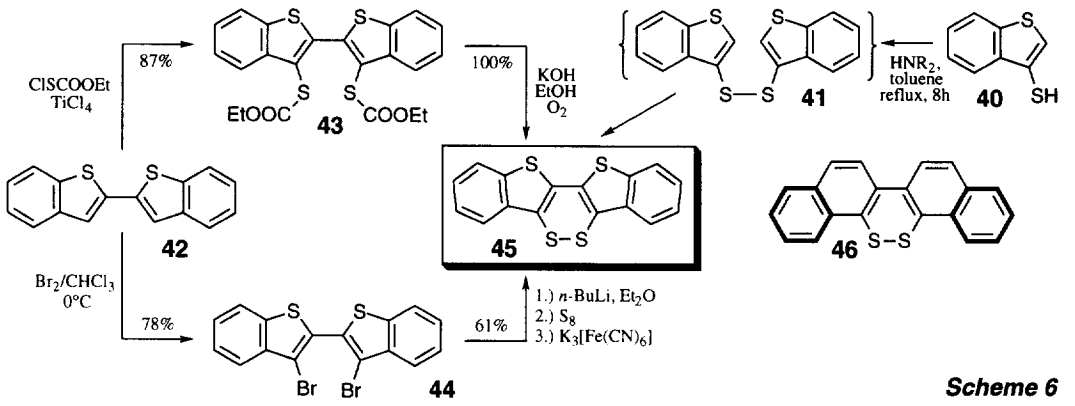
Due to the remarkable stability towards sulfur extrusion a smooth oxidation of **32** with *m*-chloroperbenzoic acid to produce sulfoxides is possible as exemplified by the transformation to **35b**. Oxidation at the dithiin sulfur is clearly evidenced by decolourization. At this time NMR detection of two diastereomers and, thus, hindrance of 1,2-dithiin ring inversion failed: no doubling of the proton signals in CD_2Cl_2 could be observed up to -95°C in contrast to the behaviour of the diborneno anellated 1,2-dithiin sulfoxide.[22a] Reduction of the S,S-bond of **32** was easily achieved with sodium borohydride affording the dithiols **36**. After dissolving the latter in sodium hydroxide solution (via **37**) they could be smoothly reoxidized to the 1,2-dithiins **32** as well as reacted with benzyl chloride to yield the benzylthio derivatives **38** and with acetic anhydride to give the acetylthio compounds **39**. These derivatives allow regeneration of **37** by debenzylation with sodium in liquid ammonia or saponification, respectively, and hence transformation back to **32** as described above.

4. Bis(benzo[4,5]thieno)[3,2-*c*:2',3'-*e*][1,2]dithiin (45)

This deep red crystalline compound represents an isomer of dithioxothioindigo. With respect to the questionable existence of the latter structure type,[19] we previously reported the unusual and not general formation of **45** from benzo[*b*]thiophene-3-thiol (**40**) via disulfide **41**, as well as its structure and properties (*Scheme 6*).[22b] Its reactivity is, on the whole, comparable with that of **32**. Here two further complementary routes based on specific thio functionalization at the 3- and 3'-position of 2,2'-bis(benzo[*b*]thienyl) (**42**) are described. In the first sequence electrophilic substitution with ethoxycarbonylsulfenyl chloride furnished the thiocarbonic ester **43**,[23] which was then saponified to the corresponding dithiolate and the latter in-situ oxidized by air. The second route parallels the synthesis of **32**, namely by bromination to produce **44**, followed by bromo lithium exchange, in-situ thiolation with the aid of elemental sulfur and oxidation.

The absorption of **45** with λ_{max} = 467 nm is bathochromicly shifted relative to that of the mono-benzo[*b*]-thieno anellated 1,2-dithiin **26** and the dithieno anellated 1,2-dithiins **32**. On the other hand, **45** may be regarded as a sulfur bridged 3,6-diphenyl-1,2-dithiin which shows an equal long-wave absorption around λ_{max} = 464 nm, whilst the iso-π-electronic di-naphtho anellated 1,2-dithiin **46** (formally considered as an ethylene

bridged 3,6-diphenyl-1,2-dithiin) is quite colourless in spite of the similarity of its non-planar molecular structure with that of **45** (for more detailed informations see ref.[22b]).



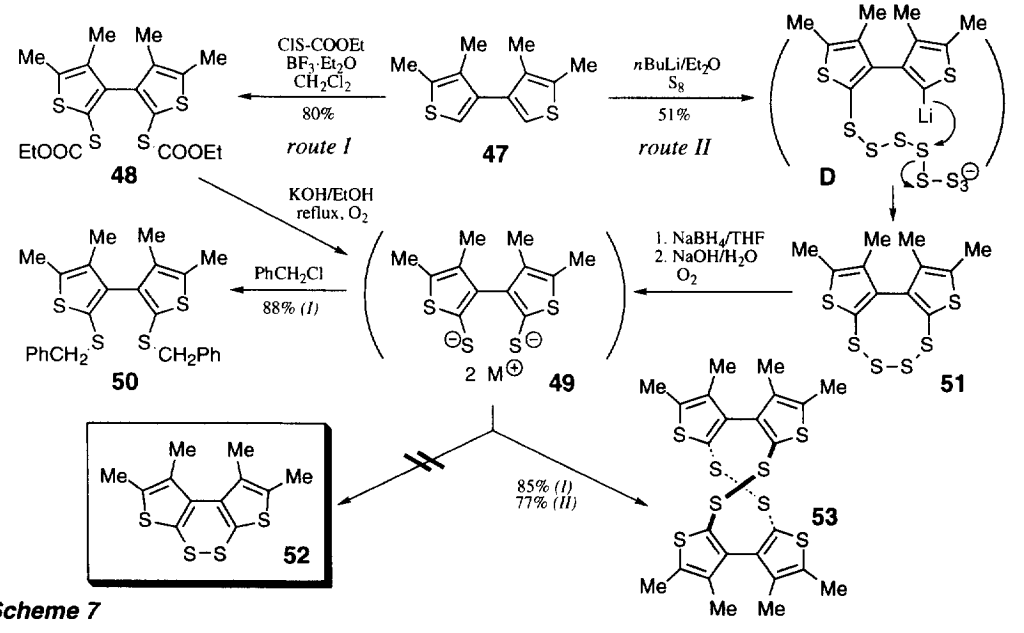
Scheme 6

5. Supplement: Anomalies regarding the isomeric thieno[2,3-*c*] anellated series

It should be noted that in the various attempts to prepare the isomeric thieno[2,3-*c*] anellated 1,2-dithiins failure occurred in the final stage due to other reactions. Whether π-electronic or steric reasons are implicated is, a yet, unclear. This situation is illustrated by the following two examples.[24]

a) Attempted synthesis of 2,3,4,5-tetramethyldithieno[2,3-c:3',2'-e][1,2]dithiin (**52**)[25]

In contrast to the unproblematical synthesis of **32b** (cf. Scheme 4), its "iso-anellated" counterpart **52** was not obtained under analogous conditions (*Scheme 7*). Its synthesis by in-situ oxidation of the dithiolate intermediate **49** failed due to the formation of the 12-membered cyclic bis-disulfide **53**. Nevertheless, **52** does appear to exist in the gas phase, as indicated by the base peak in the electron impact mass spectrum. Only via this species can the majority of fragmentations be explained.



Scheme 7

The key intermediate **49** was accessible by two routes: in *route I* tetramethyldithienyl **47** was treated with ethoxycarbonylsulfenyl chloride[23] to give the bis-thiocarbonic ester **48**, which was subsequently saponified. The presence of **49** (not isolated) was proved by its transformation to the di(benzylthio) derivative **50**.

In *route II* thiolation of **47** via lithiation and reaction with elemental sulfur surprisingly furnished the 8-membered cyclic tetrasulfide **51**, possibly via **D**. By subsequent treatment with sodium boranate, **51** suffered elimination of two sulfur atoms to yield again **49**.

A reason that **52** could not be formed may be seen in steric overcrowding of the methyl groups in 3- and 3'-positions of the 2,2'-dithienyl unit.[26] According to force field calculations[27] (*Figure 2*) the energy minimum of **52** exists at a torsion of the dithienyl unit (C=C–C=C) of 39.8° and of the disulfide unit (C-S-S-C) at 63.0°, whilst that of the iso-anellated counterpart **32b** requires essentially less torsion with dihedral angles C=C–C=C at 27.5° and C–S–S–C at 55.4° in accord with the values from the X-ray analysis of **32b** (C=C–C=C at 21.5° and C–S–S–C at 52.5°).[19] Reducing the C=C–C=C torsion angle of **52** to that of **32b**, the van der Waals' radii of the methyl groups overlap dramatically. On the other hand, with increasing torsion of both thiophene planes an energetically disadvantageous deformation of the bond angles within the dithiin moiety results and, consequently, the formation of the 12-membered ring **58** competes successfully. A disadvantage of the formation of **52** is also revealed by comparison of the dithienyl models **54** and **55** as equivalents of the corresponding dithiolate precursors: the energy content of **54** depends on rotation around the connecting C,C bond substantially more than that of **55** and approaches its minimum not before 50°.

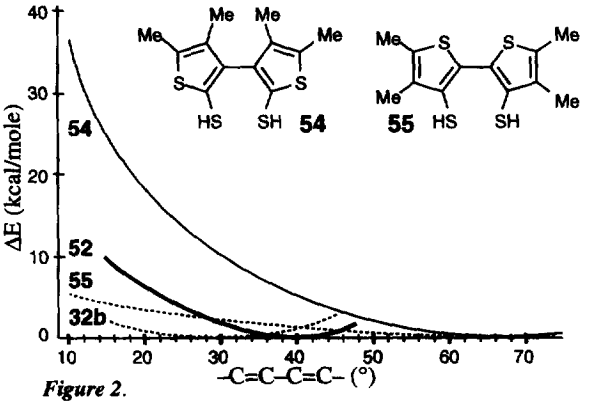


Figure 2.
Dependence of energy on torsion of the thiophene units around the connecting C,C-bond.

According to X-ray elucidation of **53** (*Figure 3*),[25,28] strain has been minimized, the C-S-S-C dihedral angle is about 93-94°. Furthermore, the thiophene rings within the 2,2'-dithienyl unit are twisted towards each other at about 114-115° and the both dithienyl units are opposite directed to each other. Apparently the methyl groups in 3- and 3'-positions of the dithienyl units are sufficiently far from each other.

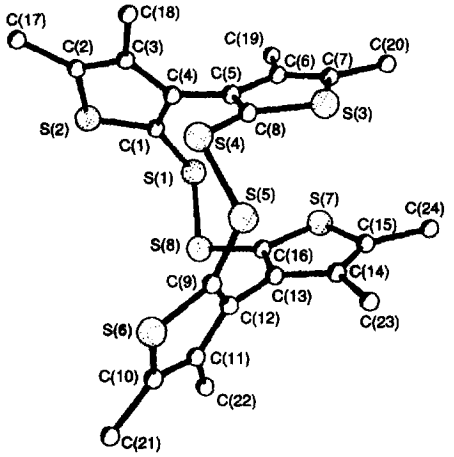
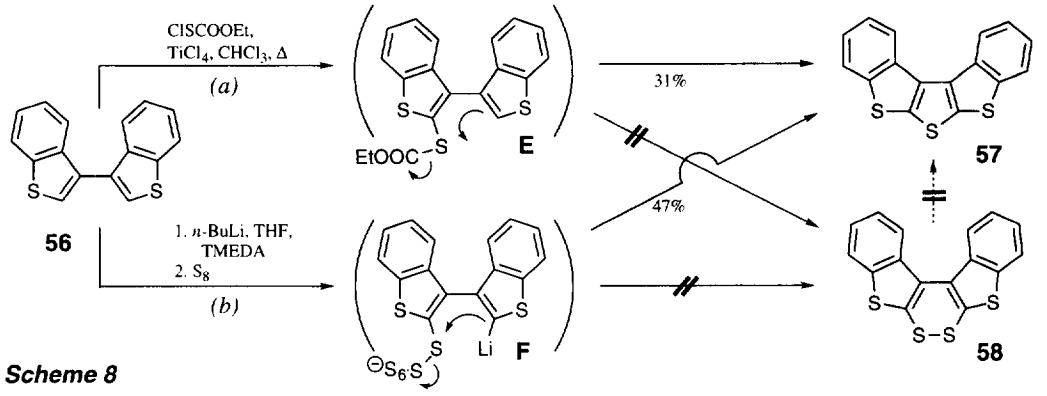


Figure 3.
X-ray crystal structure of 2,3,4,5,10,11,12,13-octamethyl-1,6,7,8,9,14,15,16-octathiatetracyclopenta[a,c,g,i]cyclododecene (**53**). – Important bond lengths [Å] and angles [°]: S(1)-S(8) 2.067(2), S(4)-S(5) 2.062(2), S(1)-C(1) 1.747(5), S(8)-C(16) 1.750(5), C(12)-C(13) 1.485(7), C(9)-C(12) 1.366(7); C(1)-S(2)-S(8) 107.09(16), S(1)-S(8)-S(16) 105.55(17); C(1)-S(4)-S(8)-S(16) -93.13(21), C(8)-S(4)-S(5)-C(9) -93.93(23), C(1)-C(4)-C(5)-C(8) -117.28(57), C(9)-C(12)-C(13)-C(16) -114.41(61), C(3)-C(4)-C(5)-C(6) -114.70(54), C(11)-C(12)-C(13)-C(14) -114.62 (58).

b) Attempted access to bis(benzo[4,5]thieno)[2,3-c:3',2'-e][1,2]dithiin (**58**)

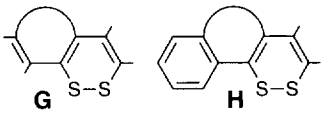
Instead of this dithiin the corresponding bis(benzothieno)thiophene **57**[29] resulted when di(benzothienyl) **56**[30] was reacted in analogy to the synthesis of the iso-anellated dithiin **45** (*Scheme 8*). In contrast to the latter only one sulfur atom was incorporated into **56** by ethoxycarbonylthiolation via **E** as well as by lithiation and subsequent thiolation via **F**. A path producing dithiin **58** in the primary step and subsequent conversion to **57** seems to be highly improbable due to the general stability of di-anellated 1,2-dithiins towards sulfur extrusion (cf. ref.[1], ref.[22a] especially p. 13250).



Scheme 8

Conclusions

The unusual colour of 1,2-dithiin **1** (R = H) is influenced by substitution as well as anellation. Whilst unsaturated substituents R, hence, extension of the butadiene conjugation cause *bathochromic shifts*, anellated unsaturated rings effect *hypsochromic shifts* according to the abilitiy to involve the double bonds of 1,2-dithiin into their π-system, as exemplified by the extreme case of areno anellation.



In contrast to the latter, thieno[3,2-*c*] anellated 1,2-dithiins of type **A** and **B** (**5a-c**, **26**, **32a-c**, **45**) show light absorption in the "normal" range, confirming an essentially decreased π-delocalization or enhanced double bond character of the thiophene ring, respectively. Here obviously the thieno anellated system resembles rather a bridged alkenyl or aryl substituted 1,2-dithiin as illustrated by **G** and **H**.

Access to the isomeric thieno[2,3-*c*] anellated series, represented by **52**, **58**, and **66** (see ref.[24]), was mainly prevented by competing reactions in the final stage. For the alternative formation of the 12-membered cyclic bis-disulfide **53** instead of the 1,2-dithiin **52**, steric reasons may be mainly responsible.

Experimental Part

NMR spectra:Varian Unity 500 (^{1}H: 499.84 MHz, ^{13}C: 125.71 MHz), Bruker WP 200 (^{1}H: 200.13 MHz, ^{13}C: 50.3327 MHz), Bruker AC 80 (^{1}H: 80.13 MHz, ^{13}C: 20.149 MHz). ^{1}H and ^{13}C NMR spectra were recorded with TMS as standard (in ppm). – MS: Varian MAT CH6, AMD Intectra 402 (70 eV). – IR: Carl Zeiss Jena Specord 71 and 75; Perkin-Elmer Spectrum 1000. – UV: Beckman DK-2A; Perkin-Elmer Lambda 16 – Column chromatography (CC): silica gel 60 [70-230 and 230-400 mesh (Merck)]. – HPLC: Merck Hitachi L-4000 (UV detector). – Melting points: Hot stage microscope (Boetius M; all temperatures quoted are not corrected). – X-ray analyses: Diffractometer STADI4 (Stoe, MoK$_\alpha$ radiation, $3 < 2\Theta < 54°$). – Elemental analyses: Carlo Erba (automatic apparatus).

3-Benzylthiothiophene (**7**). – 8.2 g (50 mmol) **6** were added during 15 min at -60°C to a solution prepared from 37.5 mL (60 mmol) of 1.6 M *n*-BuLi/*n*-hexane and 50 mL THF. After stirring for further 30 min at -50°C to -70°C, 11.7 g (47.5 mmol) dibenzyl disulfide dissolved in THF was added at -70°C over 5 min and the mixture was stirred for further 30 min. Water was added, the aqueous phase extracted twice with ether, the combined layers washed with 2N KOH solution and finally evaporated. After distillation (b.p. 95°C/10^{-2} Torr) the colourless oil crystallized. – 7.6 g (78%); m.p. 34-35°C, identical to that prepared by benzylation of thiophene-3-thiol.[11]

3-Benzylthio-2-formylthiophene (**8**). – A solution of 4.6 g (19.6 mmol) **7** in 20 mL abs. DMF was added dropwise to the reagent obtained from 2.15 mL (28 mmol) DMF and 2.18 mL (24 mmol) $POCl_3$. After heating 3 h at 95°C the mixture was poured into water and extracted twice with ether. The concentrated organic layer was chromatographed [cyclohexane/$CHCl_3$, subsequently $CHCl_3$ (R_f = 0.53)]. The resulting oil solidified to give colourless block-like crystals. – 3.7 g (79%); m.p. 35-36°C. – IR (KBr):$\tilde{\nu}$ = 1653 cm^{-1} (s, C=O). – ^{1}H NMR ($CDCl_3$): δ = 4.10 (s, 2 H, -SCH_2-), 7.06 (d, 1 H, aromat. H; J = 5.09 Hz), 7.17-7.28 (m, 5 H, aromat. H), 7.64 (dd, 1 H, aromat. H; J = 5.09 Hz, J = 1.1 Hz), 9.82 (d, -CHO; J = 1.1 Hz). – ^{13}C NMR ($CDCl_3$): δ = 40.2 (-SCH_2-), 127.7, 128.7, 128.7, 131.3, 134.0, 136.5. – MS (70 eV): m/z = 234 (44) [M$^+$], 201 (31)

[M^+ – SH], 173 (14) [M^+ – SH – CO], 143 (23) [M^+ – C_7H_7], 91 (100) [$C_7H_7^+$]. – $C_{12}H_{10}OS_2$ (234.3): calcd. C 61.51, H 4.30, S 27.36; found C 61.53, H 4.49, S 27.41.

3-Benzylthio-2-(2,2-dibromovinyl)thiophene (**9**). – A mixture of 6.64 g (20 mmol) CBr_4 and 30 mL abs. CH_2Cl_2 was added dropwise at 0°C to a solution of 10.48 g (40 mmol) PPh_3 in 100 mL abs. CH_2Cl_2. After 30 min a solution of 3 g (12.8 mmol) **8** in 30 mL abs. CH_2Cl_2 was added. After 1 h the mixture was partitioned between *n*-pentane/water and then treated with a solution of iodine in CH_2Cl_2 until the yellow colour persisted The separated organic layer was washed with an aqueous solution of $Na_2S_2O_3$, dried (Na_2SO_4), evaporated and the residue purified by CC ($CHCl_3$/cyclohexane 1:1). – 3 g (60%); pale yellow oil; R_f = 0.52 (cyclohexane/$CHCl_3$ 1:1). – ^{1}H NMR ($CDCl_3$): δ = 3.88 (s, 2 H, -SCH_2-), 6.94 (d, J = 5.24 Hz; 1 H, aromat. H), 7.05-7.29 (m, 5H, aromat. H), 7.40 (dd, J = 5.24 Hz, J = 0.67 Hz; 1 H, aromat. H), 7.76 (d, J = 0.67 Hz; 1 H, olef. H). – ^{13}C NMR ($CDCl_3$): δ = 41.4 (-CH_2-), 88.0 (=CBr_2), 126.1, 127.4, 128.5, 128.9, 129.9, 131.7, 132.5, 137.4, 139.2 (11 C, aromat./olefin. C). – MS (70 eV): m/z = 390 (9) [M^+], 311, 309 (20, 19) [M^+ – Br], 299 (3) [M^+ – C_7H_7], 220, 218 (16, 15) [M^+ – Br – C_7H_7], 91 (100) [$C_7H_7^+$]. – $C_{13}H_{12}Br_2S_2$ (390.2): calcd. C 40.02, H 2.58, Br 40.96, S 16.43; found C 40.05, H 2.83, Br 40.50, S 16.71.

3-Benzylthio-2-ethinylthiophene (**10**).

a) By debromination of **9**: A 1.6 M solution of *n*-BuLi (10.25 mL; 16.4 mmol) was added dropwise with stirring at -78° to a solution of 3.2 g (8.2 mmol) **9** in 60 mL abs. THF and the mixture stirred for a further 1 h at this temperature. After the addition of 10 mL water the aqueous phase was saturated with NaCl and extracted with ether. The combined organic layers were dried ($MgSO_4$), evaporated (40°C) and the residue purified by CC (*n*-hexane/benzene 4:1; R_f = 0.21). – Pale yellow oil; 465 mg (25%). – IR (cap.): ν̃ = 3300 (s, ≡CH), 2100 (m, C≡C) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 3.58 (s, 1 H, ≡CH), 4.11 (s, 2 H, -SCH_2-), 6.77 (d, J = 5.3 Hz; 1 H, aromat. H), 7.12 (d, J = 5.3 Hz; 1 H, aromat. H), 7.21-7.27 (m, 5 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 39.5 (SCH_2-), 75.9 (*C*≡CH), 85.7 (≡CH), 121.3, 126.5, 127.2, 128.5, 128.9, 130.2, 137.5, 137.5 (10 C, aromat. C). – MS (70 eV): m/z = 230 (23) [M^+], 197 (2) [M^+ – SH], 153 (4) [M^+ – C_6H_5], 139 (2) [M^+ – C_7H_7], 91 (100) [$C_7H_7^+$]. – $C_{13}H_{10}S_2$ (230.3): calcd. C 67.79, H 4.38, S 27.84; found 67.60, H 4.62, S 27.14.

b) By deprotection of **12**: A solution of 3.64 g (12.6 mmol) **12** together with a catalytic amount of NaOH in 50 mL toluene was refluxed for 1 h with removal of the acetone by distillation. After cooling to room temperature and filtration, the filtrate was evaporated and the residue purified by CC (CH_2Cl_2/MeOH, 40:1; R_f = 0.71). Data above.

3-Benzylthio-2-(3-hydroxy-3-methyl-1-butynyl)thiophene (**12**). – The mixture obtained from 3.7 g (13 mmol) **11**[11b,14], 247.5 mg (1.3 mmol) CuI, 91 mg (0.13 mmol) bis(triphenylphosphine)palladium dichloride, 330 mg (1.26 mmol) PPh_3 and 2.1 mL (21 mmol) 2-methyl-3-butyn-2-ol in 50 mL NEt_3 was refluxed with stirring until TLC-indicated termination of the reaction. After cooling to room temperature the material was filtered and the separated solid washed with NEt_3 and ether. The residue on evaporation of the filtrate was purified by dissolution in CH_2Cl_2, filtration and finally CC (CH_2Cl_2/ MeOH 40:1, R_f = 0.58) of the oil obtained from the evaporated filtrate. – Yellow oil; 3.4 g (91%). – IR (CCl_4): ν̃ = 3600, 3520-3300 (m, OH), 2213 (m, C≡C) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.60 [s, 6 H, -$C(CH_3)_2$], 2.02 (s, 1 H, OH), 4.09 (s, 2 H, -SCH_2-), 6.8 (d, J = 5.12 Hz; 1 H, aromat. H), 7.1 (d, J = 5.12 Hz; 1 H, aromat. H), 7.19-7.25 (m, 5 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 31.3 [$C(CH_3)_2$], 39.5 (-SCH_2-), 65.8 [$C(CH_3)_2OH$], 74.5 [C≡$C(CH_3)_2OH$], 102.1 [C≡$C(CH_3)_2OH$], 122.20. 125.93, 127.16, 128.43, 128.83, 130.27, 136.25, 137.67 (10 C, aromat. C). – MS (70 eV): m/z = 288 (36) [M^+], 273 (6) [M^+ – CH_3], 255 (7) [M^+ – CH_3 – H_2O, 229 (12) [M^+ – $C(CH_3)_2OH$], 197 (3) [M^+ – C_7H_7], 91 (100) [$C_7H_7^+$]. – $C_{16}H_{16}OS_2$ (288.4): calcd. C 66.63, H 5.59, S 22.23; found C 66.79, H 5.31, S 22.20.

(*Z*)- and (*E*)-3-Benzylthio-2-(2-benzylthiovinyl)thiophene (***Z*-13/*E*-13**). – The solution obtained from 1.32 g (10.7 mmol) phenylmethanethiol, 130.7 mg (2.3 mmol) KOH and 40 mL DMF was stirred for 20 min under argon. Then 2.23 g (9.7 mmol) **10** were added which caused colour change to reddish brown. After stirring for 180 min the mixture was poured into 150 mL water, extracted twice with AcOEt and the organic layer washed twice with water and brine. The residue obtained on evaporation was purified by CC (cyclohexane/ $CHCl_3$ 1:1, R_f = 0.52). – Dark yellow oil; 2.99 g (87%); *Z*/*E* = 66:34. – ^{1}H NMR ($CDCl_3$): δ = 3.80 (s, -SCH_2-, *E*), 3.85 (s, -SCH_2-, *Z*), 3.93 (s, -SCH_2-, *E*), 4.03 (s, -SCH_2-, *Z*), 6.15 (d, J = 10.65 Hz; 1 H, olefin. H; *Z*), 6.53 (d, J = 15.47 Hz; 1H, olefin. H; *E*), 6.69 (d, J = 15.47 Hz; 1 H, olefin. H; *E*), 6.77 (d, J = 5.16 Hz; 1 H, CH-thiophene, *E*), 6.86 (d, J = 5.13 Hz; 1 H, CH-thiophene, *Z*), 6.89 (d, J = 10.65 Hz; 1 H, olefin. H; *Z*), 7.06-7.38 (m, 22 H, aromat. H, *Z*/*E*). – ^{13}C NMR ($CDCl_3$): δ = 37.2 (-SCH_2-, *E*), 39.49 (-SCH_2-, *Z*), 41.2 (-SCH_2-, *E*), 41.3 (-SCH_2-, *Z*), 118.5, 119.7, 122.0, 124.3, 124.7, 125.4, 126.5, 126.9, 127.0, 127.3, 127.4, 128.3, 128.30,

128.5, 128.6, 128.6, 128.8, 128.8, 128.8, 128.9, 131.7, 132.6, 136.9, 137.2, 137.9, 138.0, 141.4, 143.3 (36 C, aromat./olefin. C, *Z/E*). – MS (70 eV): m/z = 354 (6) [M^+], 263 (11)[$M^+ - C_7H_7$], 214 (6) [$M^+ - C_7H_7 - H - HSCH_3$], 123 (11) [$M^+ - C_7H_7 - H - HSCH_3 - C_7H_7$], 91 (100) [$C_7H_7^+$]. – $C_{20}H_{18}S_3$ (354,5): calcd. C 67.75, H 5.12, S 27.13; found C 67.30, H 5.22, S 27.03.

(*Z*)- and (*E*)-3-Acetylthio-2-(2-acetylthiovinyl)thiophene (*Z*-14/*E*-14). – 3.25 mL (19.78 mmol) N,N-dimethyl-1-naphthylamine was added dropwise to a mixture of 160 mg (26 mmol) lithium (tapes) and 40 mL abs. THF at -45°C to -55°C under an argon atmosphere with stirring (colour change to dark green) and stirring continued for 3.5 h at the noted temperature (generation of 0.5 M solution of LDMAN). At -78°C a solution of 1.52 g (4.3 mmol) ***Z*-13/*E*-13** in 5 mL THF was added and stirring continued for 90 min. Subsequently excessive (freshly distilled) AcCl and finally water were added to the mixture which then was evaporated i. vac. The residue was dissolved in ether, the extract washed with 5% H_2SO_4, water and aqueous $NaHCO_3$ solution. The residue obtained on evaporation was purified by CC (benzene, R_f = 0.22). The resulting oil crystallized. – Pale yellow irregular crystals; 444 mg (40%); m.p. 45-60°C; 66:34 *Z/E*-mixture. – IR (KBr): $\tilde{\nu}$ = 1700 (s, C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 2.37 (s, 3 H, CH_3, *E*), 2.38 (s, 3 H, CH_3, *Z*), 2.39 (s, 3 H, CH_3, *E*), 2.47 (s, 3 H, CH_3, *Z*), 6.85 (d, J = 16.1 Hz; 1 H, olefin. H; *E*), 6.91 (d, J = 10.91 Hz; 1 H, olefin. H; *E*), 6.97 (d, J = 10.91; 1 H, olefin. H; *Z*), 7.02 (d, J = 5.17 Hz; 1 H, aromat. H; *Z*), 7.14 (d, J = 16.1 Hz; 1 H, olefin. H; *E*), 7.25 (d, J = 4.32 Hz, 1 H, aromat. H; *E*), 7.45 (d, J = 5.17 Hz; 1 H, aromat. H; *Z*), 1 H of *E* covered. – ^{13}C NMR ($CDCl_3$): δ = 29.5, 29.9, 30.5, 31.1 (4 CH_3), 117.6, 119.5, 119.8, 121.6, 122.5, 123.3, 124.4, 126.3, 132.4, 132.8, 142.7, 143.8 (12 C, olefin./aromat. C, *Z/E*), 189.9, 191.5, 193.0, 193.2 (4 C, C=O, *Z/E*). – MS (70 eV): m/z = 258 (36) [M^+], 216 (39) [$M^+ - CH_2CO$], 215 (39) [$M^+ - CH_3CO$], 174 (44) [$M^+ - 2\ CH_2CO$], 173 (49) [$M^+ - CH_2CO - CH_3CO$], 172 (6) [$M^+ - 2\ CH_3CO$], 141 (94) [$M^+ - 2\ CH_2CO - SH$], 140 (100) [$M^+ - CH_2CO - CH_3CO - SH$]. – $C_{10}H_{10}O_2S_3$ (358.4): calcd. C 46.49, H 3.90, S 37.23; found C 46.81, H 4.21, S 36.85.

Thieno[3,2-*c*][1,2]dithiin (5a). – A solution of 730 mg (2.83 mmol) **14** (*Z/E*-mixture) in 17.4 mL abs. 5% methanolic KOH (2.1 mol KOH pro Ac group) was stirred under argon for 1 h at ambient temperature. After cooling to -30°C a solution of 718.3 mg (2.83 mmol) I_2 in 10 mL MeOH was added dropwise. After continued stirring for further 30 min 25 mL water and 30 mL ether were added. The aqueous layer was extracted additionally with ether. The combined ether phases were washed (5% H_2SO_4, 5% $NaHCO_3$, water) and evaporated; the residue was purified by CC (*n*-hexane, R_f = 0.26). – Red oil; 159 mg (50% relative to **Z-14**). – UV/Vis (MeCN): λ_{max} (lg ε) = 206 (4.076), 297 (3.741), 441 (2.630) nm. – ^1H NMR ($CDCl_3$): δ = 6.14 (d, J = 9.23 Hz; 1 H, olefin. H), 6.78 (pseudo-t, J = 9.53 Hz, J = 5.13 Hz; 2 H, thieno/olefin. H), 7.27 (d, J = 5.13 Hz; 1 H, thieno H). – ^{13}C NMR ($CDCl_3$): δ = 118.0, 125.4, 126.1, 126,1 (4 CH, aromat./olefin. C), 124.4, 136.6 (2 C_{qu}, aromat. C). – $C_6H_4S_3$ (172.3): calcd. C 41.83, H 2.34; found C 41.54, H 2.69. – Transformation to **thieno[3,2-*b*]thiophene (15)**: 10 mg **5a** in 1ml DMSO-d_6 (NMR tube) were exposed to daylight, after about 120 min ^1H NMR: δ = 7.43 (pseudo-t, J = 5.13 Hz, J = 1.47 Hz; 2 H, aromat. H), 7.65 (pseudo-t, J = 5.13 Hz, J = 1.47 Hz; 2 H, aromat. H); cf. comparable shifts and coupling constants in ref.[31] δ [$(CD_3)_2CO$] = 7.55, 7.43; J = 5.25 Hz, 1.55 Hz).

3-Benzylthiobenzo[*b*]thiophene (17). – A 3-lithiobenzo[*b*]thiophene solution was prepared according to ref.[10c] by the addition of 2.13 g (10 mmol) **16** in 10 mL ether to 6.5 mL of a 1.6 M *n*-BuLi solution (10.5 mmol) in 50 mL abs. ether at -78°C and stirring continued at this temperature for 30 min. – *Method a*: To this solution was added 320 mg (10 mmol) S_8 in two portions within 5 min. After stirring for 2 h at -78°C 1.71 g (10 mmol) $PhCH_2Br$ in 10 mL ether was added to the mixture, stirring was continued for 3 h at room temperature and then heated under reflux for a further 8 h. The organic phase was washed with water, dried (Na_2SO_4) and evaporated. The resulting yellow oil solidified at -20°C and was recrystallized from AcOEt/EtOH (1:2); 1.1 g (43%). – *Method b*: A solution of 2.46 g (10 mmol) $(PhCH_2)_2S_2$ in 50 mL abs. ether was added dropwise with stirring to the above-mentioned 3-lithiobenzo[*b*]thiophene solution at -78°C and stirring was continued at this temperature for 90 min. After quenching by means of 10 mL water, warming to room temperature and the further addition of 20 mL water the washed and dried organic phase was evaporated. The residue was recrystallized from MeOH; 1.75 g (68%). – Colourless plates; m.p. 53-54°C. – ^1H NMR ($CDCl_3$): δ = 4.01 (s, 2 H, $-SCH_2-$), 7.13 (m, 2 H, Ph-H), 7.21 (m, 4 H, Ph-H, H^2), 7.38 (m, 2 H, H^5, H^6), 7.83 (m, 1H), 7.90 (m, 1 H, H^4; H^7). – MS (70 eV): m/z = 256 (38) [M^+], 223 (10), [$M^+ - SH$], 121 (5) [$C_6H_5CS^+$], 91 (100) [$C_7H_7^+$]. – $C_{15}H_{12}S_2$ (256.4): calcd. C 70.27, H 4.72, S 25.01; found C 70.21, H 4.74, S 25.02.

3-Benzylthio-2-iodobenzo[*b*]thiophene (18). – A solution of 3 g (11.7 mmol) **17** in 35 mL ether was added dropwise with stirring to a solution prepared from 7.57 mL (12.87 mmol) 1.7 M *t*-BuLi/pentane in 25 mL abs.

ether at -78°C. After stirring for a further 45 min, the solution was diluted with 70 mL abs. THF and a solution of 3.56 g (14.04 mmol) I_2 in 10 mL THF was added dropwise over 5 min at -70°C to -75°C. After warming to -40°C the mixture was stirred for 45 min and a solution of 1.2 g $Na_2S_2O_3$ in 12 mL water was added. The separated and washed organic phase was evaporated and the residue recrystallized from MeOH. – Pale pink needles; 3.27 g (73%). – ^{1}H NMR ($CDCl_3$): δ = 3.92 (s, 2 H, -SCH_2-), 7.00-7.05 (m, 2 H, -$CH_2C_6H_5$), 7.12-7.17 (m, 3 H, -$CH_2C_6H_5$), 7.27-7.31 [m, 2 H, aromat. H (benzo)], 7.69-7.74 [m, 1 H, aromat. H (benzo)], 7.79-7.84 [m, 1 H, aromat. H (benzo)]. – ^{13}C NMR ($CDCl_3$): δ = 40.0 (-SCH_2-), 94.7 (=C-I), 121.7, 123.4, 124.7, 124.9, 127.1, 128.3, 129.0, 132.9, 137.2, 139.0, 143.3 (13 C, aromat. C). – MS (70 eV): m/z = 382 (86) [M^+], 291 (9) [$M^+ - C_7H_7$], 255 (36) [M^+ - I], 222 (30) [M^+ – I – SH], 91 (100) [$C_7H_7^+$]. – $C_{15}H_{11}IS_2$ (382.3): calcd. C 47.13, H 2.90, S 16.77; found C 47.13, H 2.96, S 17.15.

3-Benzylthio-2-(3-hydroxy-3-methyl-1-butynyl)benzo[*b*]thiophene (19). – The mixture prepared from 3.17 g (8.29 mmol) **18**, 7.9 mg (0.041 mmol) CuI, 58.2 mg (0.083 mmol) bis(triphenylphosphine)palladium dichloride, 1.3 mL (13.4 mmol) 2-methyl-3-butyn-2-ol and 20 mL NEt_3 was stirred under exclusion of air at ambient temperature for 2.5 h. The mixture was filtered, the wet cake washed with NEt_3 and ether, the combined filtrates evaporated and the residue purified by CC [*n*-hexane/AcOEt (1:1); R_f = 0.56]. – Pale yellow viscous oil; 2.75 g (97.9%). – IR ($CHCl_3$): ν = 3613 [s, OH (free)], 3550-3140 [m, broad (assoc.)] cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.60 (s, 6 H, CH_3), 2.06 (s, 1 H, OH), 4.04 (s, 2 H, -SCH_2-), 7.05-7.12 [m, 2 H, aromat. H (Ph)], 7.14-7.21 [m, 3 H, aromat. H (Ph)], 7.35-7.42 [m, 2 H, aromat. H (benzo)], 7.69-7.74 [m, 1 H, aromat. H (benzo)], 7.85 [dd, J = 6.4 and 3.0 Hz; 1 H, aromat. H (benzo)]. – ^{13}C NMR ($CDCl_3$): δ = 31.1 (CH_3), 39.7 (-SCH_2-), 65.7 [$C(CH_3)_2OH$], 75.1 [$C{\equiv}CC(CH_3)_2OH$], 103.6 [$C{\equiv}CC(CH_3)_2OH$], 122.2, 123.4, 124.9, 125.9, 127.0, 127.2, 128.3, 128.9, 130.4, 137.9, 138.6, 139.5 (14 C, aromat. C). – MS (70 eV): m/z = 338 (100) [M^+], 279 (34) [$M^+ - C(CH_3)_2OH$], 247 (9) [$M^+ - C_7H_7$], 91 (57) [$C_7H_7^+$]. – $C_{20}H_{18}OS_2$ (338.4): calcd. C 70.97, H 5.36, S 18.94; found C 70.62, H 5.63, S 18.77.

3-Benzylthio-2-ethynylbenzo[*b*]thiophene (20). – A mixture of 2.72 g (8.05 mmol) **19**, 70.1 mg (1.75 mmol) NaOH and 18.6 mL toluene was heated for 75 min at 115-120°C with stirring with removal of acetone by distillation. The filtrate was evaporated and the residue purified by CC [*n*-hexane/$CHCl_3$ (4:1), R_f = 0.31]. – Pale yellow prisms; 0.92 g (40.7%); m.p. 43-44°C. – IR (KBr): ν = 3251 (m, ≡CH), 2084 (w, C≡C) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 3.65 (s, 1 H, ≡CH), 4.09 (s, 2 H, -SCH_2-), 7.09-7.14 [m, 5 H, aromat. H (Ph)], 7.32-7.42 [m, 2 H, aromat. H (benzo)], 7.69-7.74 [m, 1 H, H (benzo)], 7.79-7.84 [m, 1 H, H (benzo)]. – ^{13}C NMR ($CDCl_3$): δ = 39.9 (-SCH_2-), 76.4 (-*C*≡CH), 87.3 (-C≡*C*H), 122.2, 123.7, 125.0, 126.18, 126.21, 127.1, 128.3, 128.9, 132.0, 137.6, 138.7, 139.5 (14 C, aromat. H). – MS (70 eV): m/z = 280 (16) [M^+], 279 (64) [M^+ – H], 203 (8) [M^+ – Ph], 189 (8) [$M^+ - C_7H_7$], 145 (16) [$M^+ - C_7H_7$ – CS], 91 (100) [$C_7H_7^+$]. – $C_{17}H_{12}S_8$ (280,.): calcd. C 72.82, H 4.31, S 22.87; found C 72.58, H 4.54, S 22.56.

Nucleophilic addition of $PhCH_2SH$ to 20: After stirring a mixture prepared from 0.18 mL (1.53 mmol) $PhCH_2SH$, 20 mg (0.37 mmol) KOH and 6.5 mL abs. DMF in an argon atmosphere for 20 min at room temperature, 390 mg (1.39 mmol) **20** were added (colour change to dark green). The mixture was stirred for a further 5.5 h at this temperature, then poured into 25 mL water and extracted with AcOEt. The evaporation residue was recrystallized and the mother liquor chromatographed. – a) *From recrystallization* [*n*-hexane/AcOEt (1:1)]: **(*E*)-3-Benzylthio-2-(2-benzylthiovinyl)benzo[*b*]thiophene (*E*-21)**; 297.4 mg (53%); ocher-yellow plates; m.p. 95-96°C. – ^{1}H NMR ($CDCl_3$): δ = 3.76 (s, 2 H, -SCH_2-), 3.91 (s, 2 H, -SCH_2-), 6.65 (d, J = 15.5 Hz; 1 H, olefin. H), 6.76 (d, J = 15.5 Hz; 1 H, olefin. H), 6.92-6.99 (m, 2 H, phenyl-H), 7.11-7.18 (m, 3 H, phenyl-H), 7.26-7.39 (m, 7 H, phenyl-H and benzo-H^5, H^6), 7.66-7.71 (m, 1 H, benzo-H), 7.81-7.85 (m, 1 H, benzo-H). – ^{13}C NMR ($CDCl_3$): δ = 37.0, 40.4 (-SCH_2-), 119.4, 120.9, 122.1, 122.8, 124.8, 125.0, 127.1, 127.5, 128.2, 128.7, 128.82, 128.85, 128.87, 136.6, 137.0, 138.1, 141.4, 147.0 (22 C, aromat. and olefin. H). – MS (70 eV): m/z = 404 (10) [M^+], 313 (80) [$M^+ - C_7H_7$], 279 (2) [$M^+ - C_7H_7 - H_2S$], 222 (15) [$M^+ - 2\ C_7H_7$], 190 (33) [$M^+ - 2\ C_7H_7 - S$], 91 (100) [$C_7H_7^+$]. – $C_{24}H_{20}S_3$ (404.6): calcd. C 71.24, H 4.98, S 23.77; found C 71.16, H 5.12, S 23.77. – b) *From chromatography* [*n*-hexane/CH_2Cl_2 (3:1)]: 1. fraction (R_f = 0.33), 17 mg (3%) ≡ ***E*-21**; 2. fraction (R_f = 0.29), turbid yellow oil, 90 mg ≡ 12% ***Z*-21** (characterization below) + 4% ***E*-21** (NMR indication); 3. fraction (R_f = 0.20), pale yellow oil, 60 mg (8%) ≡ **3-benzylthio-2-[2,2-bis(benzylthio)ethyl]benzo[*b*]thiophene (22).** – ^{1}H NMR ($CDCl_3$): δ = 3.00 [d, J = 7.2 Hz; 2 H, -*CH*$_2$-CH($SCH_2Ph)_2$], 3.57 [t, J = 7.2 Hz; 1 H, -*CH*-($SCH_2Ph)_2$], 3.62 [d, J = 13.1 Hz; 2 H, -CH(S*CH*$_2$Ph)$_2$], 3.71 [d, J = 13.1 Hz; 2 H, -CH(S*CH*$_2$Ph)$_2$], 3.72 (s, 2 H, =C-SCH_2Ph), 6.81-6.86 (m, 2 H, phenyl-H), 7.06 -7.15 (m, 13 H, phenyl-H), 7.21-7.34 (m, 2 H, benzo-H), 7.67-7.71 (m, 1 H, benzo-H), 7.81-7.85 (m, 1 H, benzo-H). – ^{13}C NMR ($CDCl_3$): δ = 29.7 [*CH*$_2$-CH($SCH_2Ph)_2$], 35.3 [CH(S*CH*$_2$Ph)$_2$], 39.2

(=C-S*C*H$_2$Ph), 50.8 [*C*H(SCH$_2$Ph)$_2$], 122.4, 122.8, 124.5, 124.6, 127.0, 128.3, 128.5, 128.7, 128.9, 129.1, 137.6, 138.1, 138.4, 140.1, 147.4 (26 C, aromat. C; 1 signal covered). – MS (70 eV): m/z = 528 (3) [M$^+$], 437 (25) [M$^+$ – C$_7$H$_7$], 405 (3) [M$^+$ – C$_7$H$_7$ – S], 313 (35) [M$^+$ – C$_7$H$_7$ – S – C$_7$H$_7$ –H], 259 (97) [CH(SCH$_2$Ph)$_2^+$], 223 (7) [M$^+$ – 3 C$_7$H$_7$ – S], 191 (20) [M$^+$ – 3 C$_7$H$_7$ – 2 S], 91 (100) [C$_7$H$_7^+$]. – $C_{31}H_{28}S_4$ (528.8): calcd. C 70.41, H 5.34, S 24.25; found C 70.17, H 5.50, S 24.23.

3-Benzylthio-2-benzylthioethynylbenzo[*b*]thiophene (23)

a) From **18**. – 1.) The synthesis of **benzylthioethyne** based on ref.[18]: A solution of 6.44 mL (54.8 mmol) PhCH$_2$SH in 82 mL THF was added dropwise over 20 min to a vigorously stirred suspension of 3.3 g (82.28 mmol) KH in 73 mL abs. THF. Stirring was continued until termination of gas evolution (about 90 min). After cooling to -50°C 5.48 mL (61.01 mmol) trichloroethene in 55 mL THF was added dropwise to the mixture over 10 min and finally 0.145 mL (3.61 mmol) MeOH was added. Stirring was continued for further 90 min at room temperature (termination of gas liberation). Subsequently 75.4 mL (0,121 mmol) of a 1.6 M solution of *n*-BuLi in *n*-hexane was added dropwise over 35 min to the reaction mixture at -70°C. After a further 30 min at this temperature and warming up to -40°C, 18 mL MeOH were added. The mixture was poured at room temperature into 220 mL of a saturated aqueous NH$_4$Cl solution and extracted three times with each 150 mL *n*-pentane. The evaporation residue was distilled under reduced pressure. – 5.06 g (62%), yellow oil; b.p. 72-75°C/1 Torr. – Physical data accord with those previously reported.[4b,32] – 2.) To a mixture of 23.65 g (61.9 mmol) **18** and 150 mL NEt$_3$ under an inert gas atmosphere were added successively 235 mg (1.234 mmol) CuI, 434 mg (0.618 mmol) Pd(PPh$_3$)$_2$Cl$_2$ and 9.62 g (64.98 mmol) benzylthioethyne (s. above). a bulky solid precipitated immediately. After stirring for 2.5 h at room temperature a further portion of 6.41 g (43.3 mmol) benzylthioethyne was added and after stirring for 2 h at 60°C, 200 mg (0.285 mmol) Pd(PPh$_3$)$_2$Cl$_2$ was added. Stirring was continued for 3.5 h at this temperature. The mixture was allowed to stand overnight at room temperature, a further amount of 2.75 g (18.58 mmol) benzylthioethyne added and stirring continued for 3 h at 60°C. The mixture was filtered and the filtrate evaporated. The residue was purified by CC [*n*-hexane/CH$_2$Cl$_2$ (4:1); R$_f$ = 0.20] and finally by recrystallization (MeOH/ AcOEt). – Pale yellow needles; 20.28 g (81%; can be increased by using excess benzylthioethyne); m.p. 57-58°C.

b) From **20**. – To a solution of 0.71 g (2.53 mmol) **20** in 10 mL abs. THF was added dropwise with stirring and inert gas protection at -60 to -70°C 1,6 mL of a 1.6 M *n*-BuLi/*n*-hexane solution. After stirring for further 20 min 81.2 mg (2.532 mmol) elemental sulfur was added in portions and the mixture stirred for 1 h at -15°C (complete disappearance of sulfur). At 0°C a further portion of 25 mg (0.78 mmol) sulfur and after 3 h at 0°C 0.30 mL (2.53 mmol) PhCH$_2$Br were added. After standing overnight at room temperature, the mixture was poured into water, extracted with ether and the organic layer evaporated. Recrystallization (MeOH/ AcOEt) and CC [*n*-hexane/CHCl$_3$ (3:1)] of the mother liquor afforded 580 mg (57%). – IR (KBr): $\tilde{\nu}$ = 2141 cm^{-1} (C≡C). – ^{1}H NMR (CDCl$_3$): δ = 3.98 (s, 2 H, -SCH$_2$-), 4.04 (s, 2 H, -SCH$_2$-), 7.04-7.16 (m, 5 H, aromat. H), 7.26-7.41 (m, 7 H, aromat. H), 7.66-7.70 (m, 1 H, aromat. H), 7.76-7.80 (m, 1 H, aromat. H). – ^{13}C NMR (CDCl$_3$): 39.7 (-SCH$_2$-), 40.9 (-SCH$_2$-), 87.1, 90.8 (*C*≡*C*), 122.1, 123.5, 124.9, 125.9, 127.0, 127.3, 127.9, 128.2, 128.7, 128.9, 129.1, 130.7, 136.3, 137.7, 138.7, 139.6 (20 C, aromat. C). – MS (70 eV): m/z = 402 (100) [M$^+$], 311 (96) [M$^+$ – C$_7$H$_7$], 278 (92) [M$^+$ – C$_7$H$_7$ – SH], 267 (30) [M$^+$ – C$_7$H$_7$ – CS], 234 (13) [M$^+$ – C$_7$H$_7$ – SH – CS], 91 (94) [C$_7$H$_7^+$]. – $C_{24}H_{18}S_3$ (402.6): calcd. C 71.60, H 4.51, S 23.89; found C 71.84, H 4.44, S 23.96.

Addition of (*n*-Bu)$_3$SnH to 23: A solution of **23** (515 mg, 1.28 mmol) in 5.8 mL abs. toluene under an argon atmosphere was treated with 15 mg (0.013 mmol) Pd(PPh$_3$)$_4$ and then 0.36 mL (1.34 mmol) of (*n*-Bu)$_3$SnH was added dropwise. The mixture was stirred for 1 h at 0°C and then for a further 1 h at room temperature. The mixture was evaporated and the residue chromatographed [*n*-hexane/CH$_2$Cl$_2$ (4:1)]: Yellow oil; 850 mg (96%); mixture of **(*E*)-3-benzylthio-2-[2-benzylthio-2-(tri-*n*-butyl)stannylvinyl]benzo[*b*]thiophene (24a)** and **(*E*)-3-benzylthio-2-[1-benzylthio-2-(tri-*n*-butyl)stannylvinyl]benzo[*b*]thiophene (24b)** in a 79:21 ratio (NMR indication). – Isolation of **24a** as first fraction; ^{1}H NMR (CDCl$_3$): δ = 0.92 (t, J = 7.3 Hz; 9 H, 3 CH$_3$), 1.08 [t, J = 8.2 Hz; ^{2}J(Sn–H) = 50.3 Hz; 6 H, SnCH$_2$-], 1.37 (pseudo-sext, J = 7.3 Hz; 6 H, 3 -CH$_2$-C*H*$_2$-CH$_3$), 1.58 (nontuplet, J = 8.0 Hz; 6 H, Sn-CH$_2$-C*H*$_2$-), 3.86 (s, 2 H, -SCH$_2$-), 4.06 (s, 2 H, -SCH$_2$-), 6.97-6.99 (m, 2 H, aromat. H), 7.12-7.14 (m, 3 H, aromat. H), 7.23-7.38 (m, 7 H, aromat. H), 7.39 [s, ^{3}J(Sn–H) = 53.7 Hz (derived from satellite signals); 1 H, olefin. H],[33] 7.76 (d, J = 7.8 Hz; 1 H, benzo-H), 7.91 (d, J = 7.8 Hz; 1 H, benzo-H). – ^{13}C NMR (CDCl$_3$): δ = 12.1 [^{1}J(^{117}Sn–C) = 321.1 Hz, ^{1}J (^{119}Sn–C) = 335.1 Hz, -Sn-CH$_2$-], 13.7 (-CH$_3$), 27.4 [^{3}J(Sn–C) = 61.8 Hz, -*C*H$_2$-CH$_3$], 28.9 [^{2}J(Sn–C) = 20.0 Hz, -Sn-CH$_2$-*C*H$_2$-], 40.6 (thienyl-S-CH$_2$-), 41.5 [^{3}J(Sn–C) = 17.0 Hz; =C–S–*C*H$_2$-], 122.2, 122.8, 124.1, 124.5, 124.9, 126.9, 127.4, 128.3, 128.6,

128.8, 129.0, 130.9 [^2J(Sn–C) = 42.9 Hz; olefin. CH], 136.8, 138.0, 139.3, 139.7, 145.3, 146.3 (22 C, aromat. + olefin. C). – MS (70 eV): m/z = 694 (0.3) [M^+], 637 (30) [M^+ – Bu], 603 (22) [M^+ – C_7H_7], 546 (9) [M^+ – Bu – C_7H_7], 455 (9) [M^+ – Bu – 2 C_7H_7], 291 (67) [$SnBu_3^+$], 235 (30) [$SnBu_2H^+$], 179 (35) [$SnBuH_2^+$], 91 (100) [$C_7H_7^+$]. – $C_{36}H_{46}S_3Sn$ (693.6): calcd. C 62.34, H 6.69, S.13.87; found C 62.16, H 6.98, S 13.83.

Hydrolysis of 24a/24b producing (*Z*)-3-benzylthio-2-(2-benzylthiovinyl)benzo[*b*]thiophene (*Z*-21). – To the solution of 200 mg (0.289 mmol) of the **24a/24b**-mixture described above in 0.72 mL THF were added 0.14 mL water gradually along with 145.4 mg (1.15 mmol) oxalic acid dihydrate. The resulting two-phase system was stirred for 22 h at room temperature, then for 4.5 h at 50°C and finally 3 h under reflux. The mixture was then poured into a dilute aqueous $NaHCO_3$ solution, extracted with $CHCl_3$ and purified by CC [*n*-hexane/CH_2Cl_2 (3:1); R_f = 0.24]. – Pale yellow prisms; 82.4 mg (71%); m.p. 98-100°C (*n*-hexane/AcOEt). – ^1H NMR ($CDCl_3$): δ = 3.82 (s, 2 H, -SCH_2-), 4.06 (s, 2 H, -SCH_2-), 6.27 (d, J = 10.7 Hz; 1 H, olefin. H), 6.95-7.03 (m, 3 H, olefin. H + phenyl-H), 7.11-7.18 (m, 3 H, phenyl-H), 7.27-7.41 (m, 7 H, aromat. H), 7.78-7.93 (m, 2 H, benzo-H). – ^{13}C NMR ($CDCl_3$): δ = 39.7, 40.6 (-SCH_2-), 119.0, 122.3, 122.9, 123.5, 124.7, 124.8, 126.9, 127.5, 128.2, 128.3, 128.7, 128.8, 129.0, 137.0, 137.9, 138.8, 140.0, 145.2 (22 C, aromat. C + olefin. C). – MS (70 eV): m/z = 404 (29) [M^+], 327 (10) [M^+ – Ph], 313 (91) [M^+ – C_7H_7], 222 (12) [M^+ – 2 C_7H_7], 190 (19) [M^+ – 2 C_7H_7 – S], 91 (100) [$C_7H_7^+$]. – $C_{24}H_{20}S_3$ (404.6): calcd. C 71.24, H 4.98, S 23.77; found C 70.99, H 4.60, 23.58.

(*Z*)-3-Acetylthio-2-(2-acetylthiovinyl)benzo[*b*]thiophene (25). – A solution of 5.40 g (13.35 mmol) ***Z*-21** in 90 mL THF was added dropwise with stirring over 1 h at -78°C to a solution of LDMAN, prepared from 460 mg (66.27 mmol) Li and 11.44 mL (69.55 mmol) N,N-dimethyl-1-naphthylamine in 150 mL THF at -45°C to -55°C. After further stirring at this temperature for 45 min, 2.6 mL MeOH and subsequently 5.72 mL (80.44 mmol) AcCl were added to the mixture. The reaction was completed by stirring for 20 min at room temperature. The mixture was then poured into dilute aqueous H_2SO_4/ice and extracted with ether. The evaporation residue was recrystallized from *n*-hexane/AcOEt. – Colourless prisms; 2.07 g (50%); m.p. 112-112.5°C. – IR (KBr): ν = 1708 cm^{-1} (s, C=O). – ^1H NMR ($CDCl_3$): δ = 2.42 (s, 3 H, -CH_3), 2.51 (s, 3 H, -CH_3), 7.12 (d, J = 11.0 Hz; 1 H, olefin. H), 7.20 (d, J = 11.0 Hz; 1 H, olefin. H), 7.38 (pseudo-quint-d, J = 7.4 and 1.4 Hz; 2 H, H^5/H^6 at ring system), 7.73 (d,d, J = 7.3 and 1.6 Hz; 1 H, H^4 or H^7 at ring system), 7.83 (d,d, J = 7.1 and 1.5 Hz; 1 H, H^4 or H^7 at ring system). – ^{13}C NMR ($CDCl_3$): δ = 30.1, 31.1 (2 C, CH_3), 119.1, 120.2, 120.9, 122.4, 123.0, 125.3, 125.7, 139.2, 139.4, 144.7 (10 C, aromat. + olefin. C), 189.8, 192.9 (2 C, C=O). – MS (70 eV): m/z = 308 (31) [M^+], 266 (29) [M^+ – CH_2CO], 223 (33) [M^+ – CH_2CO – CH_3CO], 191 (100) [M^+ – CH_2CO – CH_3CO – S]. – $C_{14}H_{12}O_2S_3$ (308.4): calcd. C 54.52, H 3.92, S 31.19; found C 54.72, H 4.08, S 31.01.

Benzo[4,5]thieno[3,2-*c*][1,2]dithiin (26). – A solution of 1.99 g (6.45 mmol) **25** in methanolic KOH [1.52 g (27.1 mmol) KOH, 36.5 mL MeOH) was stirred for 50 min at room temperature. After the addition of 50 mL MeOH at -30°C, the mixture was treated dropwise with a solution of 1.64 g (6.452 mmol) I_2 in 35 mL MeOH. After stirring for 15 min at this temperature, the solution was neutralized with the aid of 2% HCl/water, then diluted with 100 mL water and extracted with $CHCl_3$. The evaporation residue was recrystallized from *n*-hexane. All operations were performed with rigorous exclusion of daylight. – Brick red leaflets; 1.14 g (80%); m.p. 84-85°C. – UV/Vis (MeCN): λ_{max} (lg ε) = 289 (3.71), 309 (3.69), 459 (2.68) nm. – ^1H NMR ($CDCl_3$): δ = 6.34 (d, J = 9.3 Hz; 1 H, olefin. H), 6.86 (d, J = 9.3 Hz; 1 H, olefin. H), 7.33 (t, J = 7.5 Hz; 1 H, H^7 or H^8), 7.41 (t, J = 7.5 Hz; 1 H, H^7 or H^8), 7.69 (d, J = 7.8 Hz; 1 H, H^6 or H^9), 7.77 (d, J = 8.3 Hz; 1 H, H^6 or H^9). – ^{13}C NMR ($CDCl_3$): δ = 118.4, 121.1, 122.5, 123.0, 125.0, 125.4, 126.5, 136.41, 136.43, 139.1 (10 C, aromat. + olefin. C). – MS (70 eV): m/z = 222 (100) [M^+], 190 (51) [M^+ – S], 177 (24) [M^+ – CHS], 158 (9) [M^+ – 2 S], 146 (44) [M^+ – S – CS], 102 (13) [M^+ – S – 2 CS]. – $C_{10}H_6S_3$ (222.3): calcd. C 54.02, H 2.72, S 43.26; found C 53.98, H 2.48, S 42.82. – Sulfur extrusion yielding **benzo[4,5]thieno[3,2-*b*]thiophene (27)**: A solution of 200 mg (0.899 mmol) **26** in 10 mL acetone was exposed to daylight with stirring (12 h). After 3 to 4 h the solution became turbid and a flocculent precipitate separated. After evaporation and CC (*n*-hexane) of the residue 77.3 mg (45%) **27** (R_f = 0.24) was isolated [also isolated was 8 mg (28%) of sulfur, R_f = 0.51]. – Pale yellow prisms (EtOH); m.p. 86-87°C (84.5-86°C)[34a]. – ^1H NMR: ref.[34b]. – MS: ref.[34c].

4,4',5,5'-Tetraphenyl-2,2'-dithienyl (29c). – A solution of 2.36 g (10 mmol) **28c** in 40 mL abs. ether was added to 6.9 mL of a 1.6 M *n*-BuLi solution (11 mmol *n*-BuLi) and 10 mL abs. ether, and the mixture heated under reflux for 2 h. After cooling to -70°C and addition of 2 g (15 mmol) anhydrous $CuCl_2$ under an argon atmosphere the mixture was stirred at this temperature for 4 h. The mixture was carefully hydrolyzed at 0°C with 50 mL 50% HCl. The resulting powder and the evaporation residue of the ether layer were recrystallized

from EtOH/benzene (2:1). – Deep yellow leaflets; 1.74 g (74%); m.p. 209-210°C. – ^{1}H NMR ($CDCl_3$): 7.20-7.34 (m, 22 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 127.0, 127.1, 127.5, 128.4, 128.5, 129.0, 12. 133.4 (C-ipso) (8 C, aromat. C), 135.5, 136.3, 137.6, 138.4 (4 C, thiophene-C). – MS (70 eV): m/z = 47 (100) [M$^+$], 235 (3) [M/2$^+$]. – $C_{32}H_{22}S_2$ (470.6): calcd. C 81.66, H 4.71, S 13.62; found C 81.46, H 4.69, S 13.64.

3,3'-Dibromo-4,4',5,5'-tetraphenyl-2,2'-dithienyl (30c). – A solution of 1.6 g (10 mmol) Br_2 in 20 mL $CHCl_3$ was added dropwise with ice cooling over 20 min to a solution of 2.25 g (5 mmol) **29c** in 50 mL $CHCl_3$. After further stirring for 15 min with ice cooling and for 45 min at room temperature, 100 mL $CHCl_3$ were added, the mixture washed with $NaHCO_3$ solution and water, and evaporated. The residue was recrystallized from benzene/EtOH (2:1). – Pale yellow needles; 2.6 g (83%); m.p. 271°C. – ^{1}H NMR ($CDCl_3$): δ = 2.75 [m_c (broad), 10 H, aromat. H], 7.37 [m_c (broad), 10 H, aromat. H]. – ^{13}C NMR ($CDCl_3$): δ = 127.8, 127.9, 128.3, 128.5, 128.9, 129.3, 129.4, 130.8 (8 C, phenyl-C), 133.4, 134.6, 136.8, 140.4 (4 C, thiophene-C). – MS (70 eV): 628 (100) [M$^+$], 314 (7) [M/2$^+$], 468 (17) [M$^+$ – 2 Br]. – $C_{32}H_{20}Br_2S_2$ (628.4): calcd. C 61.16, H 3.21, Br 25.43, S 10.20; found C 61.01, H 3.22, Br 25.44, S 9.97.

Dithieno[3,2-*c*:2',3'-*e*][1,2]dithiins 32a-c. – General procedure: 8.7 mL of a 1.6 M *n*-BuLi solution was added dropwise with stirring and under an inert gas atmosphere at -70°C to a solution of 3 mmol of **30a-c** in 200 mL ether. The mixture was stirred at this temperature for further 2.5 h (in the case of **30c** additionally for 30 min at room temperature), then a portion of 212 mg (6.6 mmol) pulverized elemental sulfur was added at once and stirring continued for 3 h. At -10 to 0°C the mixture was carefully hydrolyzed with 100 mL of 10% NaOH solution. The separated orange red solid was filtered and combined with the evaporation residue of the organic phase. The aqueous layer was treated with an aqueous 5% solution of $K_3[Fe(CN)_6]$ and the precipitate together with the other isolated solids purified.

Dithieno[3,2-*c*:2',3'-*e*][1,2]dithiin (32a). – CC [*n*-hexane/benzene (3:1), R_f = 0.43] and recrystallization from EtOH/H_2O (5:1). – Long brick red needles; 130 mg (19%); m.p. 66°C. – UV/Vis (MeCN): λ_{max} (lg ε) = 231 (3.64), 264 (3.53), 315 (3.81), 431 (2.81) nm. – ^{1}H NMR ($CDCl_3$): δ = 6.84 (d, J = 4.0 Hz; 2 H, thieno-H); 7.22 (d, J = 4.0 Hz; 2 H, thieno-H). – ^{13}C NMR ($CDCl_3$): δ = 123.8, 125.1, 126.7, 134.3, (8 C, thieno-C). – MS (70 eV): m/z = 228 (100) [M$^+$], 196 (20) [M$^+$ – S], 164 (4) [M$^+$ – 2 S], 151 (16)[M$^+$ – SH – CS]. – $C_8H_4S_4$ (228.4): calcd. C 42.08, H 1.77, S 56.16; found C 41.80. H 1.92, S 55.77.

2,3,6,7-Tetramethyldithieno[3,2-*c*:2',3'-*e*][1,2]dithiin (32b). – Recrystallization from EtOH [R_f (*n*-hexane/benzene, 3:1) = 0.52]. – Small red blocks; 545 mg (64%); m.p. 202-203°C. – UV/Vis (MeCN): λ_{max} (lg ε) = 238 (4.22, sh), 296 (4.21), 335 (4.18), 441 (3.52) nm. – ^{1}H NMR ($CDCl_3$): δ = 1.79 (s, 6 H, 2 CH_3), 1.74 (s, 6 H, 2 CH_3). – ^{13}C NMR ($CDCl_3$): δ = 12.8, 13.5 (4 CH_3), 125.3, 130.5, 131.4, 131.8 (8 C, thieno-C). – MS (70 eV): m/z = 284 (100) [M$^+$], 269 (16) [M$^+$ – CH_3], 252 (40) [M$^+$ – S], 251 (67) [M$^+$ – HS], 142 (7) [M$^+$/2]. – $C_{12}H_{12}S_4$ (284.5): calcd. C 50.67, H 4.25, S 45.08; C 50.03, H 4.47, S 45.38.

2,3,6,7-Tetraphenyldithieno[3,2-*c*:2',3'-*e*][1,2]dithiin (32c). – Recrystallization from EtOH/benzene (1:1) [R_f (*n*-hexane/benzene, 1:1) = 0.49]. – Orange red needles; 973 mg (61%); m.p. 304-306°C. – UV/Vis (MeCN): λ_{max} (lg ε) = 236 (4.08), 303 (3.79), 352 (3.64), 450 (3.09) nm. – ^{1}H NMR ($CDCl_3$): δ = 7.08-7.37 (m, 20 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 127.4, 127.6, 127.9, 128.3, 128.4, 128.9, 130.1, 130.7 (24 C, phenyl-C), 133.2, 134.5, 136.8, 138.7 (8 C, thieno-C). – MS (70 eV): m/z = 532 (100) [M$^+$], 500 (50) [M$^+$ – S], 466 (13) [M$^+$ – 2 HS], 266 (8) [M$^+$/2]. – $C_{32}H_{20}S_4$ (532.8): calcd. C 72.14, H 3.78, S 24.07; found C 71.81, H 4.04, S 23.70.

Desulfurization of 32a-c yielding dithieno[3,2-*b*:2',3'-*d*]thiophenes 33a-c. – General procedure: An initimate mixture of 1 mmol **32a-c** and 250 mg (3.9 mmol) copper powder was heated at 180-200°C, for **33c** at 300-320°C (metal bath) for 45 min. The mixture was then thoroughly extracted with hot $CHCl_3$ followed by evaporation and recrystallization (or sublimation) under reduced pressure.

Dithieno[3,2-*b*:2',3'-*d*]thiophene (33a). – Colourless needles; 92 mg (47%); m.p. 65-66°C (EtOH; ref.[35]: 66.5-67.5°C). – ^{1}H NMR ($CDCl_3$): δ = 6.92 (d, J = 8.0 Hz; 2 H, aromat. H), 7.22 (d, J = 8.0 Hz; 2 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 123.6, 125.2, 126.9, 134.3 (8 C, thieno-C). – MS (70 eV): m/z = 196 (100) [M$^+$]. – $C_8H_4S_3$ (196.3): calcd. C 48.95, H 2.05, S 49.00; found C 48.64, H 2.31, S 49.02.

2,3,5,6-Tetramethyldithieno[3,2-*b*:2',3'-*d*]thiophene (33b). – Light beige leaflets; 127 mg (50%); m.p. 206-207°C (sublim. 120°C/10 Torr). – ^{1}H NMR ($CDCl_3$): δ = 2.21 (s, 6 H, 2 CH_3), 2.44 (s, 6 H, 2 CH_3). – ^{13}C NMR ($CDCl_3$): δ = 12.9, 13.7 (4 CH_3), 125.5, 130.6, 131.5, 131.9 (8 C, thieno-C). – MS (70 eV): m/z = 252 (100) [M$^+$], 237 (46) [M$^+$ – CH_3]. – $C_{12}H_{12}S_3$ (252.4): calcd. C 57.10, H 4.79, S 38.11; found C 56.80, H 4.92, S 37.98.

2,3,5,6-Tetraphenyldithieno[3,2-*b*:2',3'-*d*]thiophene (**33c**). – Pale yellow leaflets; 345 mg (69%); m.p. 298°C (sublim. 180-190°C/8-10 Torr). – ^{1}H NMR ($CDCl_3$): 7.21-7.52 (m, 20 H, aromat. H). – MS (70 eV): m/z = 500 (100) [M$^+$]. – $C_{32}H_{20}S_3$ (500.7): calcd. C 76.76, H 4.03, S 19.21; found C 76.49, H 4.19, S 19.40.

Reaction of 32 with triethyl phosphite. – A solution of 1 mmol **32b,c** and 0.2 mL (1.3 mmol) $P(OEt)_3$ in 3 mL o-dichlorobenzene was heated under reflux until complete colour change from deep red to pale yellow (15-20 min). After cooling to room temperature the mixture was filtered through a short silica gel column (CH_2Cl_2) and the second zone isolated.

3-(Diethoxyphosphorylthio)-3'-ethylthio-4,4',5,5'-tetramethyl-2,2'-dithienyl (**34b**). – Yellow oil; 243 mg (54%); dec. at 145-150°C/1 Torr. – ^{1}H NMR ($CDCl_3$): δ = 0.98-1.47 (m, 9 H, 3 CH_3), 2.22 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 2.37 (s-broad, 6 H, 2 CH_3), 2.48-2.72 (q, J = 4.1 Hz; 2 H, -S-C*H*$_2$-CH_3), 3.73-4.22 (m, 4H, 2 -O-C*H*$_2$-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 13.8, 13.9, 14.6, 15.8, 15.9 (7 CH_3), 29.9, 63.9, 64.2, (3 -C*H*$_2$-CH_3), 130.4, 130.8, 132.4, 133.5, 133.6, 136.2, 136.6 (8 C, thienyl-C). – ^{31}P NMR (benzene, capill. D_2O): δ = 20.3. – MS (70 eV): m/z = 450 (100) [M$^+$], 390 (4) [M$^+$ – 4 CH_3], 281 (30) [M$^+$ – $PO(OEt)_2$ – S], 252 (50) [M$^+$ – $PO(OEt)_2$ – SEt]. – $C_{18}H_{27}O_3PS_4$ (450.6): calcd. C 47.98, H 6.04, S 28.46; found C 47.93, H 5.77, S 28.01.

3-(Diethoxyphosphorylthio)-3'-ethylthio-4,4',5,5'-tetraphenyl-2,2'-dithienyl (**34c**). – Pale yellow leaflets; 341 mg (49%); m.p. 93-95°C [EtOH/benzene (4:1)]. – – ^{1}H NMR ($CDCl_3$): δ = 0.75-1.07 (m, 9 H, 3 CH_2-C*H*$_3$), 2.08-2.27 (q, J = 4.2 Hz; -S-C*H*$_2$-CH_3), 3.23-3.73 (m, 4 H, 2 -O-C*H*$_2$-CH_3), 6.90-7.36 (m, 20 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 13.9 (-S-CH_2-*C*H$_3$), 14.5 (2 -O-CH_2-*C*H$_3$), 29.8, 63.5, 64.0 (3 -C*H*$_2$-CH_3), 120.6, 127.2, 127.7, 127.8, 127.9, 128.2, 128.4, 128.5, 128.9, 129.1, 129.3, 129.9, 130.3, 130.6, 130.7, 133.3 (24 C, phenyl-C), 134.5, 135.9, 136.2, 136.8, 138.0, 138.2, 140.2, 142.5 (8 C, thienyl-C). – ^{31}P NMR (benzene, capill. D_2O): 19.3. – MS (70 eV): m/z = 698 (100) [M$^+$], 529 (38) [M$^+$ – $PO(OEt)_2$ – S], 500 (96) [M$^+$ – $PO(OEt)_2$ – S-Et]. – $C_{38}H_{35}O_3PS_4$ (698.9): calcd. C 65.30, H 5.05, S 18.35; found C 64.99, H 5.30, S 18.22.

2,3,6,7-Tetramethyldithieno[3,2-*c*:2',3'-*e*][1,2]dithiin-4-oxide (**35b**). – A solution of 300 mg (≈ 1 mmol) 50-60% MCPBA in 15 mL CH_2Cl_2 was added dropwise at 0°C over 20 min with stirring to a solution of 284.5 mg (1 mmol) **32b** in 15 mL CH_2Cl_2 (colour change from deep red to yellow). After further stirring for 1 h at this temperature, the product was isolated by CC (CH_2Cl_2) and recrystallized from EtOH. – Yellow block-like crystals; 204 mg (68%); m.p. 230-231°C. – IR (KBr):ν̃ = 1090 (s, S=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.26 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 12.1, 12.7, 13.0, 13.5 (4 CH_3), 119.0, 125.3, 129.5, 131.6, 131.8, 132.0, 132.8, 133.7 (8 C, thieno-C). – MS (70 eV): m/z = 300 (24) [M$^+$], 284 (16) [M$^+$ – O], 252 (100) [M$^+$ – SO], 237 (40) [M$^+$ – SO – CH_3]. – $C_{12}H_{12}OS_4$ (300.5): calcd. C 47.97, H 4.03, S 42.68; found C 47.61, H 3.98, S 42.22.

Reduction of 32b,c with $NaBH_4$. – To a solution of 1 mmol **32b,c** in 10 mL benzene, 10 mL ether and 1 mL water was added under an argon atmosphere 380 mg (10 mmol) $NaBH_4$ (colour change from deep red to yellow over 5 min). After further stirring for 1 h at ambient temperature, the mixture was carefully acidified with 2 N H_2SO_4 and 20 mL benzene was added. The yellow organic layer was separated and processed. The evaporation residue was then recrystallized from a suitable solvent.

4,4',5,5'-Tetramethyl-2,2'-dithienyl-3,3'-dithiol (**36b**). – Pale yellow needles; 245 mg (86%); m.p. 160-161°C [EtOH/benzene (1:1)]. – ^{1}H NMR ($CDCl_3$): δ = 2.11 (s, 6 H, 2 CH_3), 2.35 (s, 6 H, 2 CH_3), 3.34 (s, 2 H, SH). – ^{13}C NMR ($CDCl_3$): δ = 12.8 (CH_3), 13.6 (CH_3), 125.4, 130.5, 131.5, 131.7 (8 C, thienyl-C). – MS (70 eV): m/z = 286 (75) [M$^+$], 253 (100) [M$^+$ – SH], 238 (53) [M$^+$ – SH – CH_3], 220 (96) [M$^+$ – 2 SH], 205 (17) [M$^+$ – 2 SH – CH_3], 190 (11) [M$^+$ – 2 SH – 2 CH_3]. – $C_{12}H_{14}S_4$ (286.5): calcd. C 50.31, H 4.93, S 44.76; found C 49.98, H 4.99, S 44.95.

4,4',5,5'-Tetraphenyl-2,2'-dithienyl-3,3'-dithiol (**36c**). – Yellow needles; 358 mg (67%); m.p. 245-246°C [EtOH/benzene (2:1)]. – ^{1}H NMR ($CDCl_3$): δ = 3.56 (s, 2 H, 2 SH), 7.18-7.42 (m, 20 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 124.9, 127.7, 127.9, 128.4, 128.7, 128.9, 129.1, 130.5 (24 C, aromat. C), 133.4, 135.7, 138.1, 141.7 (8 C, thienyl-C). – MS (70 eV): m/z = 534 (86) [M$^+$], 502 (100) [M$^+$ – S], 501 (93) [M$^+$ – SH], 468 (24) [M$^+$ – 2 SH], 267 (9) [M$^+$/2], 234 (18) [M$^+$/2 – SH]. – $C_{32}H_{22}S_4$ (534.8): calcd. C 71.87, H 4.15, S 23.98; found C 71.51, H 4.34, S 24.11.

Alkylation and acylation of 36. – To a freshly prepared solution of 1 mmol **36** in 20 mL aqueous 1 N NaOH (inert gas atmosphere) was gradually added 277 mg (2.2 mmol) $PhCH_2Cl$ (yielding **38**) or 224 mg (2.2 mmol) Ac_2O (yielding **39**). The separated product was filtered by suction and recrystallized.

3,3'-Bis(benzylthio)-4,4',5,5'-tetramethyl-2,2'-dithienyl (38b). – Pale yellow prisms; 289 mg (62%): m.p. 131-132°C (EtOH). – ^1H NMR ($CDCl_3$): δ = 1.99 (s, 6 H, 2 CH_3), 2.34 (s, 6 H, 2 CH_3), 3.74 (s, 4 H, 2 $PhCH_2$-S), 7.07-7.35 (m, 10 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 13.4, 13.9 (4 CH_3), 41.2 (2 CH_2-), 127.0, 128.3, 129.1, 130.6, 133.2, 134.6, 136.4, 138.0 (20 C, thienyl-C, aromat. C). – MS (70 eV): m/z = 466 (46) [M^+], 375 (44) [$M^+ - C_7H_7$], 342 (11) [$M^+ - C_7H_7 - SH$], 284 (100) [$M^+ - 2\ C_7H_7$]. – $C_{26}H_{26}S_4$ (466.73): calcd. C 66.91, H 5.61, S 27.48; found C 66.28, H 5.70, S 27.81.

3,3'-Bis(benzylthio)-4,4',5,5'-tetraphenyl-2,2'-dithienyl (38c). – Yellow prisms; 493 mg (69%); m.p. 181-182°C [EtOH/benzene (2:1)]. – ^1H NMR ($CDCl_3$): δ = 3.44 (s, 4 H, 2 $PhCH_2$-S), 6.82-7.39 (m, 30 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 40.3, (2 CH_2), 126.9, 127.3, 127.4, 128.1, 128.2, 128.3, 128.9, 129.1, 130.9, 131.2, 133.8, 136.1, 136.6, 137.3, 140.6, 141.2 (44 C, thienyl C, aromat. C). – MS (70 eV): m/z = 714 (19) [M^+], 623 (13) [$M^+ - C_7H_7$], 590 (9) [$M^+ - C_7H_7 - SH$], 558 (2) [$M^+ - C_7H_7 - 2\ SH$], 532 (100) [$M^+ - 2\ C_7H_7$]. – $C_{46}H_{34}S_4$ (715.0): calcd. C 77.27, H 4.79, S 17.94; found C 76.97, H 4.99, S 17.82.

3,3'-Bis(acetylthio)-4,4',5,5'-tetramethyl-2,2'-dithienyl (39b). – Colourless leaflets; 285 mg (77%); m.p. 120°C [EtOH/benzene (1:1)]. – IR (nujol):$\tilde{\nu}$ = 1710 (s, C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 2.04 (s, 6 H, 2 CH_3-CO), 2.23 (s, 6 H, 2 CH_3-thienyl), 2.37 (s, 6 H, 2 CH_3-thienyl). – ^{13}C NMR ($CDCl_3$): δ = 13.2, 13.9, (4 CH_3-thienyl), 29.8 (2 *C*H_3-CO), 125.0, 134.6, 134.8, 135.0, (8 thienyl-C), 194.1 (C=O). – MS (70 eV): m/z = 370 (67) [M^+], 328 (64) [$M^+ - CH_2CO$], 286 (71) [$M^+ - 2\ CH_3CO$], 253 (100) [$M^+ - 2\ CH_3CO - S$]. – $C_{16}H_{18}O_2S_4$ (370.0): calcd. C 51.86, H 4.90, S 34.61; found C 51.50, H 4.94, S 34.44.

3,3'-Di(ethoxycarbonylthio)-2,2'-di(benzo[b]thienyl) (43). – A solution of 660 mg (5 mmol) ethoxycarbonylsulfenyl chloride in 3 mL abs. $CHCl_3$ was added dropwise with ice-cooling and stirring to a solution of 660 mg (2.5 mmol) **42** [30] and 0.55 mL (5 mmol) $TiCl_4$ in 10 mL abs. $CHCl_3$ (deep violet colour). After 3 h at ambient temperature and 2 h at reflux, the mixture was poured onto 100 g ice/30 mL conc. HCl. The separated organic phase was evaporated and the crude product twice recrystallized from $EtOH/H_2O$ (8:1). – Pale yellow block-like crystals; 1.03 g (87%); m.p. 99-100°C. – IR (nujol):$\tilde{\nu}$ = 1720 (s, C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 1.21 (t, J = 4.35 Hz; 6 H, 2 CO-CH_2-*C*H_3), 4.21 (q, J = 4.33 Hz; 4 H, 2 CO-*C*H_2-CH_3), 7.25-7.58 (m, 8 aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 14.2 (CH_2-*C*H_3), 64.5 (*C*H_2-CH_3), 122.8, 123.3, 125.4, 125.8, 132,5, 136.5, 136.9, 138.5 (thienyl-C, aromat. C). – MS (70 eV): m/z = 474 (40) [M^+], 370 (46) [$M^+ - 2$ COOEt], 296 (100) [$M^+ - 2$ COOEt – S]. – $C_{22}H_{18}O_4S_4$ (474.0): calcd. C 55.70, H 3.83, S 26.98; found C 55.83, H 3.99, S 26.81.

3,3'-Dibromo-2,2'-di(benzo[b]thienyl) (44; cf. ref.[20b]). – A solution of 40 mg (4 mmol) Br_2 in 20 mL abs. $CHCl_3$ was added dropwise with stirring and ice-cooling to a solution of 532 mg (2 mmol) **42** [30]. After further stirring for 3 h at room temperature the organic layer was isolated and the evaporation residue was recrystallized from EtOH/benzene (2:1). – Pale yellow block-like crystals; 661 mg (78%); m.p. 177-178°C. – ^1H NMR ($CDCl_3$): δ = 7.31-7.61, 7.73-7.99 (ratio 1:1; 8 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 110.8, 122.2, 124.0. 125.4, 126.3, 129.4, 138.1, 139.1 (thienyl-C, aromat. C). – MS (70 eV): m/z = 424 (100) [M^+], 344 (15) [M^+ – Br], 264 (77) [$M^+ - 2$ Br]. – $C_{16}H_8Br_2S_2$ (421.8): calcd. C 45.51, H 1.91, Br 37.42, S 15.16; found C 45.39, H 2.05, Br 36.97, S 14.74.

Bis(benzo[4,5]thieno)[3,2-*c*:2',3'-*e*][1,2]dithiin (45). – *a) From* **43**: A mixture of 474 mg (1 mmol) **43**, 168 mg (3 mmol) KOH and 10 mL abs. EtOH was refluxed in an argon atmosphere for 1 h. Subsequently at room temperature a stream of air was bubbled through the mixture {alternatively treated with $K_3[Fe(CN)_6]$}. The precipitated product was recrystallized from toluene or nitromethane. Yield: 325 mg (98%) **45**. – *b) From* **44**: To a solution of 1.42 g (3 mmol) **44** in 200 mL abs. ether was added dropwise at -70°C with stirring with exclusion of air and moisture 8.7 mL of a 1.6 M *n*-BuLi solution. After further stirring at this temperature for 3 h, 212 mg (6.6 mmol) of powdered elemental sulfur was added and stirring continued for 3 h. At about 0°C the mixture was carefully treated with 100 mL 10% NaOH solution. The organic phase was evaporated to yield a first crop of the product. The aqueous phase was treated with a 5% aqueous solution of $K_3[Fe(CN)_6]$ in order to obtain further product could. Yield: 600 mg (61%). – Characterization in ref.[22b].

2,2'-Bis(ethoxycarbonylthio)-4,4',5,5'-tetramethyl-3,3'-dithienyl (48). – A solution of 0.703 g (5 mmol) of ethoxycarbonylsulfenyl chloride in 2 mL CH_2Cl_2 was added dropwise with stirring to a mixture of 0.56 g (2.5 mmol) **47** [20b], 0.4 mL (5 mmol) BF_3·Et_2O and 8 mL abs. CH_2Cl_2 at 0°C. After stirring for further 15 min at this temperature and subsequently for 2 h at room, temperature the mixture was poured into ice/HCl, and 30 mL CH_2Cl_2 was added. The separated organic layer was evaporated and the residue recrystallized from EtOH. – Colourless prisms; 800 mg (80%); m.p. 147-148°C. – IR (nujol): $\tilde{\nu}$ = 1720 (s, C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 1.21 (t, J = 4.0 Hz; 6 H, 2 O-CH_2-CH_3), 1.82 (s, 6 H, 2 thienyl CH_3), 2.41 (s, 6 H, 2 thienyl CH_3), 4.20 (q, J = 4.0 Hz; 4 H, 2 O-CH_2-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 12.9, 13.9, 14.2, (6 CH_3), 64.1 (2 CH_2), 118.3, 134.3, 139.4, 144.8 (8 C, thienyl C), 169.0 (C=O). – MS (70 eV): m/z = 430 (61) [M^+], 284 (35) [M^+ – 2 COOEt], 252 (100) [M^+ – 2 COOEt – S]. – $C_{18}H_{22}O_4S_4$ (430.6): calcd. C 50.21, H 5.15, S 29.78; found C 49.87, H 5.32, S 29.88.

2,2'-Bis(benzylthio)-4,4',5,5'-tetramethyl-3,3'-dithienyl (50). – A solution of 430 mg (1 mmol) **48** and 168 mg (3 mmol) KOH in 10 mL EtOH was heated with reflux and argon protection for about 15 min. After dilution with 15 mL water, benzyl chloride (0.275 mL, 2.2 mmol) was added. The separated oily product was purified by CC [*n*-hexane/benzene (1:1)] and the first yellow fraction isolated (R_f = 0.51). Pale yellow oil; 410 mg (88%); dec. > 170-180°C/0.5 Torr. – ^1H NMR ($CDCl_3$): δ = 1.27 (s, 6 H, 2 CH_3), 1.71 (s, 6 H, 2 CH_3), 3.88 (s, 4 H, 2 CH_2), 7.17-7.24 (m, 10 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 13.1, 13.7 (2 CH_3), 42.9 (2 CH_2), 127.5, 128.4, 128.6, 129.2 (12 C, aromat. C), 133.6, 135.5, 137.7, 142.3 (8 C, thienyl-C). – MS (70 eV): m/z = 466 (69) [M^+], 375 (7) [M^+ – C_7H_7], 310 (100) [M^+ – C_7H_7 – S – SH]. – $C_{26}H_{26}S_4$ (466.7): calcd. C 66.91, H 5.61, S 27.48; found C 66.45, H 5.81, S 27.30.

2,3,4,5-Tetramethyl-bis(thieno)[2,3-*e*:3',2'-*g*][1,2,3,4]tetrathiocine (51). – By analogy with the procedure described for **32a-c**, a solution of 670 mg (3 mmol) **47** in 200 mL ether was reacted with 6 mL of a 1.6 M *n*-BuLi solution (2 h reflux) and subsequently with 480 mg (15 mmol) pulverized elemental sulfur. – Pale yellow block-like crystals; 522 mg (51%); m.p. 231-232°C [EtOH/H_2O (7:1)]. – ^1H NMR ($CDCl_3$): δ = 1.83 (s, 6 H, 2 CH_3), 2.38 (s, 6 H, 2 CH_3). – ^{13}C NMR ($CDCl_3$): δ = 13.3, 14.1 (2 CH_3), 128.3, 134.0, 139.2, 146.8 (8 C, thieno-C). – MS (70 eV): m/z = 348 (57) [M^+], 284 (100) [M^+ – 2 S], 269 (8) [M^+ – 2 S – CH_3], 251 (50) [M^+ – 2 S – SH], 225 (16) [M^+ – 2 S – 4 CH_3]. – $C_{12}H_{12}S_6$ (348.6): calcd. C 41.35, H 3.47, S 55.18; found C 41.62, H 3.55, S 55.33.

2,3,4,5,10,11,12,13-Octamethyl-1,6,7,8,9,14,15,16-octathia-tetracyclopenta[*a,c,g,i*]cyclododecene (53).

a) From **48**: After saponification of 430 mg (1 mmol) **48** as described for **50**, a stream of air was bubbled for 2 h through the resulting mixture. The resulting powdery solid was recrystallized from DMF/H_2O (8:1). – Golden-yellow block-like crystals; 430 mg (85%); m.p. 201-202°C. – ^1H NMR ($CDCl_3$): δ = 1.80 (s [broad], 12 H, 4 CH_3), 2.33 (s [broad], 12 H, 4 CH_3). – ^{13}C NMR ($CDCl_3$): δ = 13.2, 13.4 (CH_3), 130.4, 134.1, 136.7, 140.0 (thienyl-C). – MS (70 eV): m/z = 568 (14) [M^+], 284 (100) [$M/2^+$], 269 (9) [$M/2^+$ – CH_3], 251 (46) [$M/2^+$ – SH], 237 (4) [$M/2^+$ – CH_3 – S], 224 (14) [$M/2^+$ – 4 CH_3]. – $C_{24}H_{24}S_8$ (568.9): calcd. C 50.67, H 4.25, S 45.08; found C 50.29, H 4.48, S 45.29.

b) From **51**: A solution of 105 mg (0.3 mmol) **51** in 10 mL THF was added dropwise under an argon atmosphere to a mixture of 228 mg (6 mmol) $NaBH_4$ and 20 mL THF. Violent gas evolution occurred. After stirring for further 2 h at room temperature the mixture was acidified with half-concentrated HCl and ice cooling (dec. of excessive $NaBH_4$), followed by addition of 20 mL 10% NaOH, bubbling of air for 2 h and work up as described under (a). Yield: 66 mg (77%).

Bis(benzo[4,5]thieno)[2,3-*b*:3',2'-*d*]thiophene (57). – *Method (a)* A solution of 665 mg (2.5 mmol) **56** [29] in 10 mL abs. $CHCl_3$ was treated successively with 0.55 mL (5 mmol) $TiCl_4$ (dark violet solution resulted) and then dropwise with 0.703 g (5 mmol) of ethoxycarbonylsulfenyl chloride dissolved in 3 mL abs. $CHCl_3$. After stirring at reflux for 1 h, the mixture was poured onto ice water/HCl and 30 mL $CHCl_3$ were subsequently added. The organic phase was evaporated and the resulting oil purified by CC [*n*-hexane/benzene (1:1); first pale yellow zone] and recrystallized from EtOH/benzene. – Pale yellow needles; 229 mg (31%); m.p. 198-199°C (sublimation from 140°C), cf. ref.[29a,b]. – ^1H NMR ($CDCl_3$): δ = 7.25-8.68 (m, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 123.1, 123.3, 123.9, 124.6, 132.5, 134.5, 139.5, 143.1 (aromat. C). – MS (70 eV): m/z = 296 (100) [M^+], 264 (6) [M^+ – S]. – $C_{16}H_8S_3$ (296.4): calcd. C 64.83, H 2.72, S 32.45; found C 64.39, H 2.93, S

32.59. – *Method (b)*: By analogy with the procedure described for **32a-c**, a solution of 798 mg (3 mmol) **56** and 0.69 g (6 mmol) TMEDA in 200 mL ether was reacted with 6 mL of a 1.6 M *n*-BuLi solution (2 h reflux) and subsequently with 480 mg (15 mmol) pulverized elemental sulfur. Isolation by CC (see precedingly) gave 417 mg (47%).

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References and Notes

Dedicated to Professor Roland Mayer with best wishes on the occasion of his 70th birthday

1. Part XVI: Schroth, W.; Dunger, S.; Billig, F.; Spitzner, R.; Herzschuh, R.; Vogt, A.; Jende, T.; Israel, G.; Barche, J.; Ströhl, D.; Sieler, J. *Tetrahedron* **1996**, *52*, 12677-12698.
2. Obviously based on n→σ* or σ→σ* transition, cf. quantumtheoretical calculations a) Cimiraglia, R.; Fabian, J.; Hess jr., B. A. *J. Mol. Struct. (Theochem)* **1991**, *230*, 287-293. – b) Mann, M.; Fabian, J. *ibid.* **1995**, *331*, 51-61. – Cf. also the discussion of no bond resonance with the ring-opened dithioxo valence isomer **1'** as reason (a parallelism with bathochromic shifts of the C=S group by conjugation should be suggested): c) Bohlmann, F.; Kleine, K.-M. *Chem. Ber.* **1965**, *98*, 3081-3086. – d) Moran, J. R.; Huisgen, R.; Kalwinsch, I. *Tetrahedron Lett.* **1985**, *26*, 1849-1852; cf. also: Huisgen, R.; Kalwinsch, I.; Morán, J.; Nöth, H.; Rapp, J. *Liebigs Ann./Recueil* **1997**, submitted (W.S. is indebted to Professor Huisgen for communication of the results prior to publication).
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4. To our knowledge 3,6-bis[(diphenylmethylene)amino]-1,2-dithiin-4,5-dicarbonitrile with λ_{max} = 509 nm is the „record holder".[2d] – Further examples are 3-(5-hexene-1,3-diynyl)-6-(1-propynyl)-1,2-dithiin (thiarubrine A) with λ_{max} = 490 nm: a) Koreeda, M.; Yang, W. *J. Am. Chem. Soc.* **1994**, *116*, 10793-10794; and 3-(3-buten-1-ynyl)-6-(1,3-pentadiynyl)-1,2-dithiin (thiarubrine B) with λ_{max} = 486 nm: b) Block, E.; Guo, C.; Thiruvazhi, M.; Toscano, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 9403-9404. – The formyl group gives rise to an especially strong bathochromic shift as demonstrated by **2** (R = CHO; λ_{max} = 447 nm) of about 40 nm related to **2** (R = H): c) Schroth, W.; Jordan, H.; Spitzner, R. *Tetrahedron Lett.* **1995**, *36*, 1421-1424.
5. Barber, H. J.; Smiles, S. *J. Chem. Soc.* **1928**, 1141-1149; Cossu, S.; Delogu, G.; Fabbri, D. *Org. Prep. Proced. Int.* **1991**, *23*, 455-457. – UV (MeCN): λ_{max} (lg ε) = 276 (3.79), 305 (3.46, sh) nm.
6. a) Schroth, W.; Spitzner, R.: hitherto unpublished work – b) In this connection we point out that dipyrazolo-1,2-dithiin **59**, the first claimed 1,2-dithiin representative (Michaelis, A. *Liebigs Ann. Chem.* **1908**, *361*, 251-301), was shown to be the 1,4-isomer **60**.
7. Concerning the questionable aromatic behaviour of thiophene cf. the critical review: Iddon, B. *Heterocycles* **1983**, *20*, 1127-1171.
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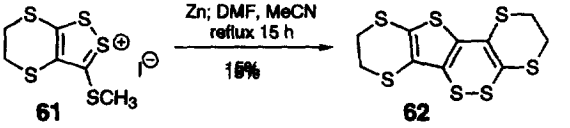
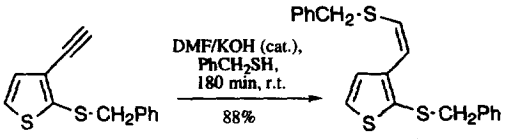
9. a) Formation of **5b,c** in low yields from a not clear reaction of substituted 1,2-dithiolium salts, 1,2-dithiol-3-thiones and cyclopropenethiones.[8] We assume that in this C_3+C_3-construction a dipolar intermediate **I** plays a key role, which will be subsequently transformed via **J** (and possibly **K**) to **5b,c** according to the following sequence [cf. interpretation in ref.[8b] (especially p. 1732)]:

b) Cf. also the formation of 3,4:6,7-bis(ethylenedithio)thieno[3,2-*c*][1,2]dithiin (**62**) by a comparable reaction of the correspondingly substituted 1,2-dithiolium salt **61** with Zn: Tanaka, M.; Ishida, T.; Nogami, T.; Yoshikawa, H.; Yasui, M.; Iwasaki, F. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1193-1199. It is noteworthy that this thieno anellated



1,2-dithiin shows its long wave absorption maximum at 472 nm.

10. Avoiding lithiation at 2-position and consecutive reactions (e.g. ring opening), cf. a) **Brandsma, L.**; Verkruijsse, H. D. *Preparative Polar Organometallic Chemistry*, Vol. 1, Springer Verlag, Berlin - Heidelberg **1987**. – b) Gronowitz, S. *Khim. Geterotsikl. Soedin.* **1994**, 1445-1481. – c) Dickinson, R. P.; Iddon, B. *J. Chem. Soc. (C)* **1971**, 3447-3454.
11. Cf. more expensive access to **6** via benzylation of thiophene-3-thiol: a) Brooks, J. W.; Howard, E. G.; Wehrle, J. J. *J. Am. Chem. Soc.* **1950**, *72*, 1289-1291. – b) Jilale, A.; Decroix, B.; Morel, J. *Chem. Scr.* **1987**, *27*, 423-428; *C.A.* **1988**, *109*, 22885p.
12. Cf. pathway by thiolation with S_8: Prim, D.; Kirsch, G. *J. Chem. Soc., Perkin Trans. I* **1994**, 2603-2606.
13. Comparable strategy based on transformation of chlorovinylaldehydes to methylthiovinylaldehydes, subsequently to methylthiovinylacetylenes and finally to thiophenes: Frejd, T.; Karlsson, J. O.; Gronowitz, S. *J. Org. Chem.* **1981**, *46*, 3132-3135.
14. a) Kellogg, R. M.; Schaap, A. P.; Harper, E. T.; Wynberg, H. *J. Org. Chem.* **1968**, *33*, 2902-2909.
15. Sabourin, E. T.; Onopchenko, A. *J. Org. Chem.* **1983**, *48*, 5135-5137.
16. As used in ref.[4b]; the "classical" use[1,3] of sodium in liquid ammonia for debenzylation of **13** gave unsatisfactory results (Birch reduction and consecutive products).
17. a) In accord with this assumption the analogous reaction of the isomer **63** afforded only the corresponding (*Z*)-addition product **64**, pale yellow oil {^{1}H NMR ($CDCl_3$): δ = 3.84 (s, 2 H, S-CH_2), 3.97 (s, S-CH_2), 6.11 (d, J = 10.98 Hz; 1 H, olefin. H), 6.51 (d, J = 10.98 Hz; 1 H, olefin. H), 7.26 (d, J = 5.61; 1 H, thiophene H), 7.02-7.36 (m, 10 H, aromat. H), 7.56 (d, J = 5.61; 1 H, thiophene H). – ^{13}C NMR ($CDCl_3$): δ = 39.0 (S-CH_2), 43.3 (S-CH_2), 119.2, 124.5, 125.5, 127.1, 127.4, 127.76, 127.8, 128.7, 128.9, 129.0, 137.3, 137.4, 142.4 (18 C, olefin. C, thieno C, aromat. C). – MS (70 eV): m/z = 354 (60) [M^+], 263 (78) [$M^+ - C_7H_7$], 172 (7) [$M^+ - 2\ C_7H_7$], 140 (6) [$M^+ - 2\ C_7H_7 - S$], 91 (100) [$C_7H_7^+$]}. – b) *G. Israel*, University Halle, unpublished results.



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21. a) $C_8H_8S_4$; red prisms, orthorhombic (obtained from EtOH/H_2O); crystal size: 0.2x0.3x0.5 mm; space group: $P2_12_12_1$ (No. 19); unit cell: a = 5.329(1), b = 13.181(2), c = 26.175(4) Å, V = 1838.5 Å^3 (the asymmetric unit contains two molecules); Z = 8; R = 0.039; $2\Theta_{max}$: 55°; unique reflections: 2795; criterion for unobserved reflections: $F_o<4\sigma(F_o)$; refined parameters: 250; scan mode: ω/Θ; μ = 9.30 cm^{-1}; program: SHELX. – b) Kempe, R.; Pink, M.; Hintzsche, E.; Schroth, W. *Z. Kristallogr.* **1993**, *208*, 148-150. – c) Further details of the structure determination (e.g. structure factors) have been deposited within the relevant database and can be accessed as Collection No. 400129 or ordered from the Fachinformationszentrum Karlsuhe, D-76344 Eggenstein-Leopoldshafen. – d) cf. also X-ray analysis of **32b** in ref.[19]).
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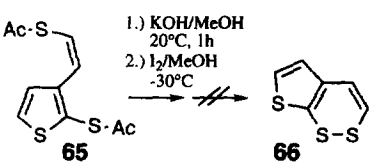
24. A third example concerns the unsuccessful synthesis of thieno[2,3-*c*][1,2]dithiin (**66**), the iso-anellated counterpart of **5a**. In contrast to the smooth transformation of *Z*-**14** to **5a** (*Scheme 2*), the analogous sequence of saponification and in-situ oxidation failed to convert the isomeric di(acetylthio) precursor **65** to **66**. Instead of that an undefined pale yellow product mixture was obtained without any UV/ Vis and NMR indication for **66**, but showing a molecular ion at m/z = 172 in the mass spectrum (presence of oligo/ polymeric disulfides?). {**65**: pale yellow crystals; m.p. 51-52°C. – IR (capill.): $\tilde{\nu}$ = 1700 (s, C=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 6.66 (d, J = 10.99



Hz; 1 H, olefin. H), 6.92 (d, J = 10.99 Hz; 1 H, olefin. H), 7.48 (d, J = 5.5 Hz; 1 H, thiophene H), 7.54 (d, J = 5.5 Hz; 1 H, thiophene H). – ^{13}C NMR ($CDCl_3$): δ = 29.6 (CH_3), 30.9 (CH_3), 118.5, 121.1, 127.7, 130.4, 130.9, 142.6 (6 C, olefin. C, thiophene C). – MS (70 eV): m/z = 258 (41) [M^+], 216 (45) [$M^+ - CH_2CO$], 174 (96) [$M^+ - 2\ CH_2CO$], 141 (100) [$M^+ - 2\ CH_2CO - HS$], 140 (84) [$M^+ - 2\ CH_2CO - H_2S$]}.

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26. Cf. analogous formation of other 12-membered cyclic bis-disufides instead of 1,2-dithiins: a) Ref.[19,25]. – b) Schroth, W.; Ströhl, D.; Thondorf, I.; Brandt, W.; Felicetti, M.; Gelbrich, T. *Tetrahedron* **1995**, *51*, 8853-8862. – c) Fanghänel, E.; Palmer, T.; Kersten, J.; Ludwigs, R.; Peters, K.; von Schnering, H. G. *Synthesis* **1994**, 1067-1071.
27. Calculations performed on a SGIndigo2 workstation (R4400 processor) using the Gridsearch Module of the SYBYL software [SYBYL (version 6.2), Tripos Associates, Inc., St. Louis, MO 63144] based on Tripos force field [Clark, M.; Cramer, R. D.; van Opdenbosch, N. *J. Comput. Chem.* **1989**, *10*, 982]. Optimizations were carried out using the Powell minimizer included in the Maximin2 routine until a cut-off for the rms energy gradient of 10^{-3} kcal mol^{-1} $Å^{-1}$ was reached. For computation of rotational barriers of the free thiols **54** and **55** the torsion angle around the interconnecting C,C-bond was varied in steps of 5° covering the range of 0° to 360°. In the case of **32b** and the (hypothetical) **52** the grid search was performed by modifying this torsion angle between 15°and 45° in steps of 1°.
28. a) $C_{24}H_{24}S_8$; yellow platelets, monoclinic; crystal size: 0.5x0.4x0.7 mm; space group: *C*12/*c*1 (No. 15); unit cell: a = 16.780(2), b = 12.701(2), c = 25.646(4) Å, V = 5337.9 $Å^3$; Z = 4; R = 0.041; $2\Theta_{max}$: 50°; unique reflections: 4939; criterion for unobserved reflections: $I_o<4\sigma(I_o)$; refined parameters: 386; scan mode: ω/Θ; μ = 3.30 cm^{-1}; program: SHELX. – b) Pink, M.; Kempe, R.; Hintzsche, E. *Z. Kristallogr.* **1993**, *208*, 151-153. – c) Further details of the structure determination (e.g. structure factors) have been deposited within the relevant database and can be accessed as Collection No. 400180 or ordered from the Fachinformationszentrum Karlsuhe, D-76344 Eggenstein-Leopoldshafen.
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