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# CYCLOCONDENSATION OF 3(2H)-BENZO[*b*]THIOPHENONE AND OXIDATION PRODUCTS OBTAINED DURING THESE REACTIONS

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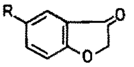
**Abstract**—The cyclocondensation of 3(2H)-benzo[*b*]thiophenone under acidic conditions has been studied. The symmetrical cyclotrimer tris(benzo[*b*]thieno)[2,3 : 2′,3′ : 2″,3″]benzene was formed and under certain conditions also a rearranged cyclotrimer, tris(benzo[*b*]thieno)[2,3 : 2′,3′ : 3″,2″]benzene. The formation of cyclotrimers was accompanied by oxidative coupling products involving the initially formed dimeric compound, 3-hydroxy-2,3-bibenzo[*b*]thienyl. During several of these reactions, a novel heterocycle, tris(benzo[*b*]thieno)[3,2-*b* : 2′,3′-*d* : 2″,3″-*f*]oxepin, was formed. The products were studied by mass spectrometry and fragmentation pathways were determined by a linked scanning technique.

In our laboratory, studies have been performed on oligomerizations of 3(2H)-benzo[*b*]furanones (3-cumaranones) (**1**) and 3(2H)-indolones (indoxyls) (**2**). 3(2H)-Benzo[*b*]furanones gave dimeric,[1,2] trimeric[2] (**3**) and tetrameric[2,3] (**4**, **5**) products depending on the conditions used. N-Methyl-3(2H)-indolone, **2b** (the O-acetate was used as precursor), gave the unsymmetrical trimer[4] (**6**) together with related higher oligomers. In view of these results, we have now investigated the cyclocondensation of 3(2H)-benzo[*b*]thiophenone (**7**) and some related reactions.

Early studies of 3(2H)-benzo[*b*]thiophenone do include some oligomerizations. Thus Bartholomäus[5] reported the formation of the dimeric condensation product **8a** when 3(2H)-benzo[*b*]thiophenone was treated with anhydrous HCl in chloroform at room temperature (similar experiments have also been reported by Krollpfeiffer[6]) or with HBr in boiling acetic acid. In the latter experiment, small amounts of a high-melting product (m.p. >330°) were obtained which were not further characterized. Later, Dalgliesh and Mann[7] reported that when treated with refluxing dichloro- or monochloroacetic acid 3(2H)-benzo[*b*]thiophenone gave two products, which were assigned the structures **8a** (present as a "bimolecular associate") and **9** based on elemental analyses, molecular weight determinations (Rast) and comparisons with oligomerization products obtained from 3(2H)-benzo[*b*]furanone.‡[1,8] The reported m.p. (225–226°) and the extremely low solubility of the purported **8a** in cold aqueous sodium hydroxide, is in striking contrast with the results of the earlier investigations,[5,6] m.p. 129.5–130° and 132–133°, respectively, and good solubility in alkaline solutions were obtained. The cyclotrimer **9** has also been reported by Proetzsch *et al.*,[9] as a product from a high-pressure condensation of 2(3H)-benzo[*b*]thiophenone. Unambiguous structural evidence for the cyclotrimer has not yet been reported.



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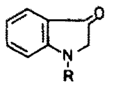

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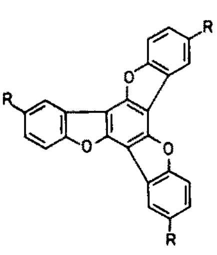

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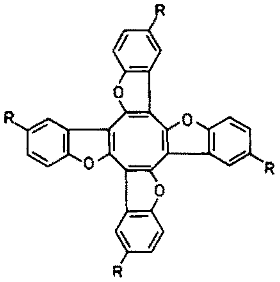

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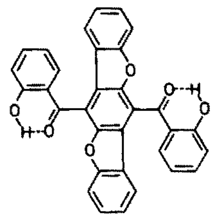

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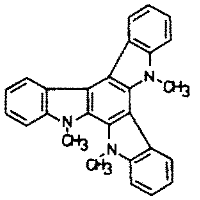

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## RESULTS AND DISCUSSION

The oligomerizations and the oxidations performed have been summarized in Scheme 1.

### *Experiments in acetic acid*/HCl

3(2H)-Benzo[*b*]thiophenone was cyclocondensed, using the conditions previously[2] applied to 3(2H)-benzo[*b*]furanone (HCl in acetic acid at 100° for 8 hr in a sealed tube). This procedure gave a complex mixture, from which a slightly yellow solid material could be collected directly from the medium. The solid was treated with dichloromethane, which left a pale rose coloured product (2% yield) having a high m.p. (>360°), and giving a molecular ion at *m*/*z* 396, thus

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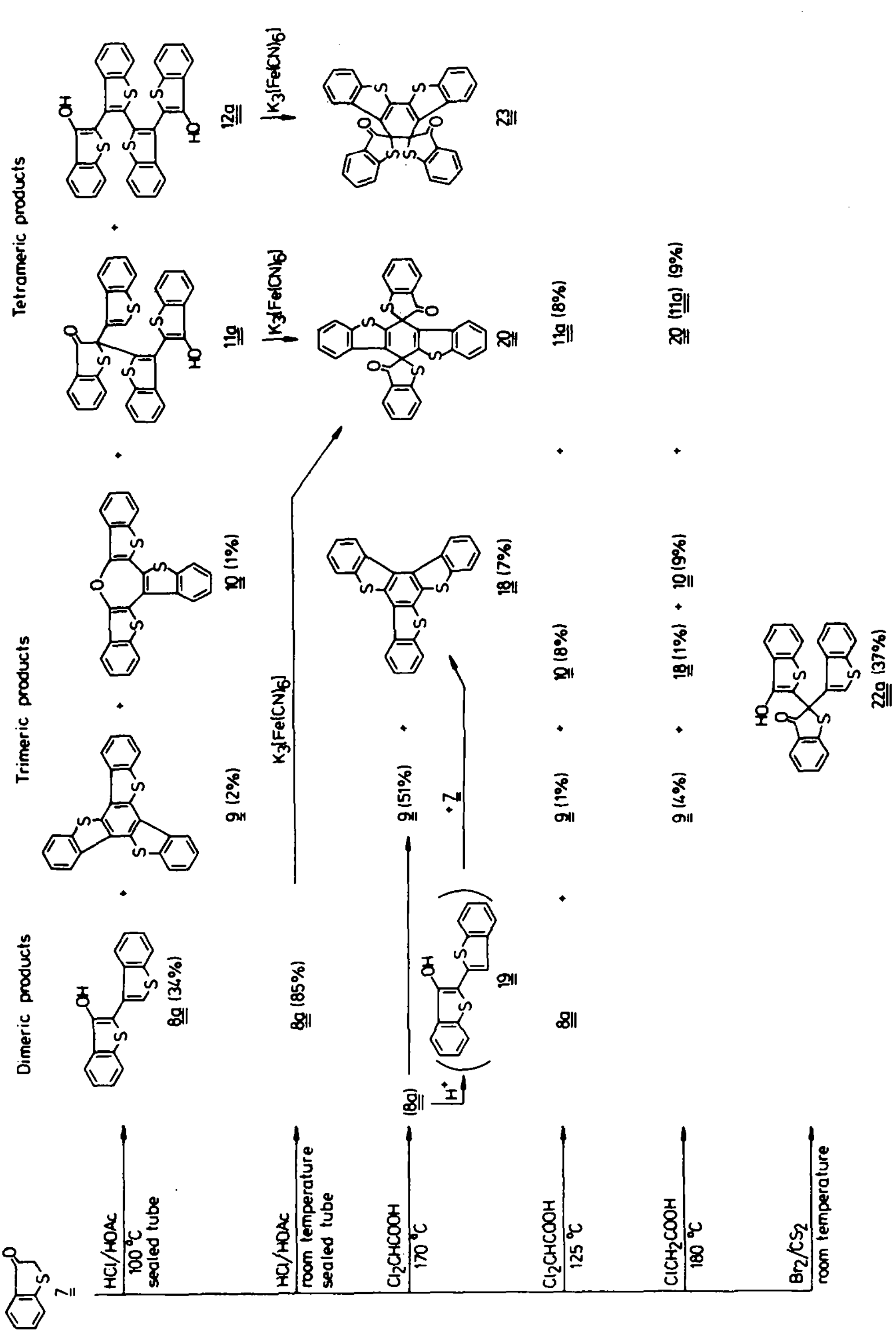
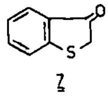
‡ The compound described as **3b** in this paper has recently been shown[2] to be **4b** as originally proposed.[1]


Dimeric products
Trimeric products
Tetrameric products
7
HCl/HOAc 100 °C sealed tube
8a (34%)
9 (2%)
10 (1%)
11a
12a
HCl/HOAc room temperature sealed tube
8a (85%)
K3[Fe(CN)6]
K3[Fe(CN)6]
K3[Fe(CN)6]
Cl2CHCOOH 170 °C
(8a)
H+
19
+7
9 (51%)
18 (7%)
20
23
Cl2CHCOOH 125 °C
8a
9 (1%)
10 (8%)
11a (8%)
ClCH2COOH 180 °C
9 (4%)
18 (1%) + 10 (9%)
20 (11a) (9%)
Br2/CS2 room temperature
22a (37%)

Scheme 1.



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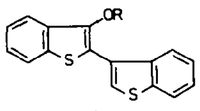
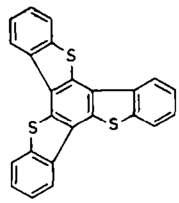


8 a R=H
b R=COCH3



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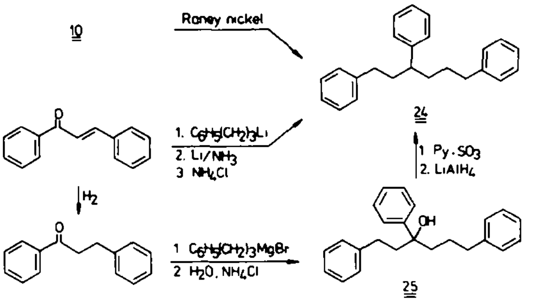
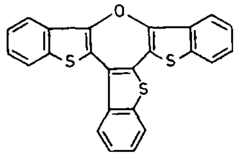


Scheme 2.



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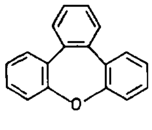

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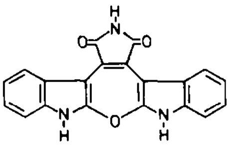


27

indicating a cyclotrimeric structure. To confirm the structure, the compound was treated with Raney Ni in dioxane, which gave a triphenylbenzene ($M^+$ = 306 daltons) shown by GC/MS to be identical with independently synthesized 1,3,5-triphenylbenzene,[13] thus proving the cyclotrimer to be tris(benzo[*b*]thieno)[2,3:2′,3′:2″,3″]benzene (**9**), which is the structure that has already been proposed.[7,9]

Evaporation of the dichloromethane extract yielded a product (1% yield) with the composition $C_{24}H_{12}OS_3$, whose mass spectrum (Fig. 1) showed a dominating molecular ion at *m/z* 412, and a strong $M^{2+}$ ion typical for a fused aromatic system. There was no characteristic absorption in the IR spectrum. These data support a tris(benzo[*b*]thieno)oxepin structure, e.g. **10**, although an alternative fusion of the benzo[*b*]thiophene moieties could not be excluded at this stage. Treatment of the oxepin with Raney Ni in dioxane gave 1,3,6-triphenylhexane (**24**) ($M^+$ = 314 daltons), whose structure was ascertained by $^{13}$C-NMR spectroscopy (the phenyl positions could unambiguously be assigned on the basis of the multiplicity of the aliphatic signals in the off-resonance spectrum) and independent syntheses. The oxepin therefore must have the structure **10**. 1,3,6-Triphenylhexane, which seems to be a new compound, was synthesized by two independent routes as outlined in Scheme 2. The tandem alkylation–reduction route was modelled from earlier work by Hall.[21] The formation of the oxepin **10** can be rationalized if an oxidative coupling,[10] *vide infra*, between 3(2H)-benzo[*b*]thiophenone and 3-hydroxy-2,3′-bibenzo[*b*]thienyl (**8a**) (present in the mixture) is assumed (to **13**), followed by protonation (to **14**), ring closure (to **15**), deprotonation and dehydration giving the oxepin **10** (Scheme 3). Structure **15** could also be regarded as the protonated form of a hemiketal. This type of intermediate has been proposed for the acid-catalyzed dehydration of 2,2′-dihydroxybiphenyls to dibenzofurans[16,17] as well as in the acid-catalyzed oligomerization of quinones.[18] The oxepin **10** is very stable and is similar to tribenz[*b,d,f*]oxepin (**26**), which showed[22] properties typical of aromatic ethers (resistant to deoxygenation when distilled with Zn dust). Relatively little is known about triarenoxepins and no general methods for their preparation are known.[23] Mass spectral data are available[22] only for **26**. Recently the interesting **27** has been isolated[24] from the slime mould *Arcyria denudata*.

Simple oxepins are usually in equilibrium with the corresponding arene oxides.[23] However, in the present case we have found no evidence for the existence of an

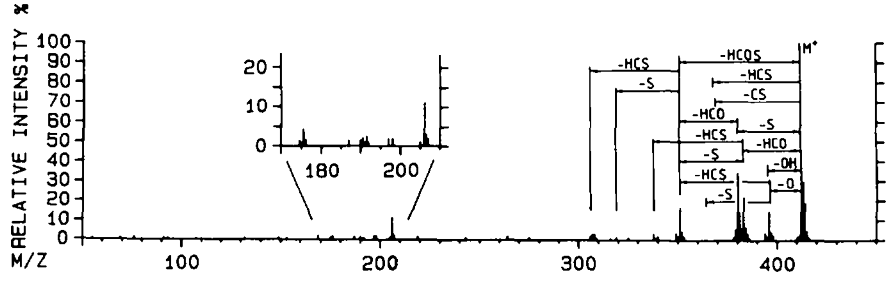
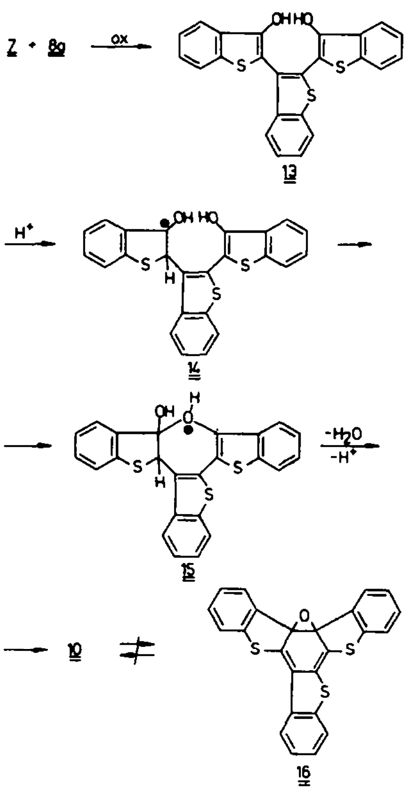


Fig. 1. Mass spectrum of tris(benzo[*b*]thieno)[3,2-*b*:2′,3′-*d*:2″,3″-*f*]oxepin (**10**), *m/z* > 50 daltons, only peaks > 0.9% of base peak, peaks on (integer + 0.5) mass excluded. Inset: peaks × 2, peaks on (integer + 0.5) mass included.



Scheme 3.

equilibrium between the structures **10** and **16** (Scheme 3).

The acetic acid filtrate from the condensation reaction of 3(2H)-benzo[*b*]thiophenone (which had yielded **9** and **10**) was poured into water, which gave further solid material. The main constituent of this material was the dimeric condensation product, 3-hydroxy-2,3′-bibenzo[*b*]thienyl (**8a**), isolated in the enol-form (IR: $\nu_{OH} = 3510\ \mathrm{cm}^{-1}$ (sharp)). The mixture also contained two yellow products, A and B. Compound A had an IR spectrum which showed absorptions due to both an OH group ($\nu = 3290\ \mathrm{cm}^{-1}$) and a CO group ($\nu = 1680\ \mathrm{cm}^{-1}$). The $^{13}$C-NMR spectrum exhibited, besides the resonances in the aromatic region, a downfield resonance at 200.75 ppm and an upfield resonance at 67.25 ppm. The signals in the off-resonance spectrum were too weak to be used to assign the multiplicity. However, the chemical shifts are in good agreement with the data obtained for **22a**, *vide infra*. The mass spectrum showed a molecular ion at *m*/*z* 562. Treatment with acetic anhydride–pyridine gave an acetate (IR: $\nu_{CO} = 1770\ \mathrm{cm}^{-1}$), with the molecular ion at *m*/*z* 604 (Fig. 2), indicating a monoacetate. The IR spectrum of compound B showed a broad O—H stretching at 3420 cm$^{-1}$ and no absorption in the C=O stretching region. When this compound was treated with acetic anhydride–pyridine an acetate (IR: $\nu_{CO} = 1780\ \mathrm{cm}^{-1}$) was obtained, giving a molecular ion at *m*/*z* 646 (Fig. 3). Two fragments ($[M-42]^+$ and $[M-84]^+$) indicated formation of a diacetate. From these data compound A has been assigned the structure 2 - (benzo[*b*]thien - 3 - yl) - 2 - (3 - hydroxy - 2,3′ - bibenzo[*b*]thienyl - 2′ - yl) - 3(2H) - benzo[*b*] - thiophenone (**11a**) and consequently structure **11b** for the monoacetate. Compound B is suggested to be 3,3‴ - dihydroxy - 2,3′ : 2′,2″ : 3″,2‴ - quaterbenzo-[*b*]thiophene (**12a**), and the diacetate then having structure **12b**. The formation of **11a** could be rationalized via a 2,2′-oxidative coupling[10] of two molecules of 3-hydroxy-2,3′-bibenzo[*b*]thienyl. A 2′,2′-coupling would then explain the formation of **12a**. The third possibility, coupling between both the 2-carbons, gives a product without any enolizable carbonyl, thus being unable to form an acetate. Compound **11a** can be stored in a pure state, but **12a** is unstable and also very difficult to purify.

Treatment of 3(2H)-benzo[*b*]thiophenone in a sealed tube without heating gave the dimer, 3-hydroxy-2,3′-bibenzo[*b*]thienyl (**8a**) as the main product (85% yield) in a pure state. This is important since the compound is not very stable. However, it can readily be handled as the acetate (**8b**). This parallels the behaviour of the oxygen analogue.[1,8] When we wanted to prepare the dimer **8a** by treating 3(2H)-benzo[*b*]thiophenone with anhydrous HCl in chloroform,[5,6] a fairly large amount of the compound proposed to have structure **11a** was obtained (11%).

The hypothesis that **11a** and **12a** are oxidative coupling products of 3-hydroxy-2,3′-bibenzo[*b*]-thienyl (**8a**) was further tested by treatment of the latter with potassium ferricyanide–potassium hydroxide, a well-established agent for oxidative coupling of phenols,[10] in dioxane–water. This procedure gave a quantitative yield of a compound, C, having a molecular ion at *m*/*z* 560 (Fig. 4). The IR spectrum had a C=O stretching at 1703 cm$^{-1}$, while 3(2H)-benzo[*b*]thiophenone has a C=O stretching at 1665 cm$^{-1}$.[15] These data suggest structures **20** and **23** as likely candidates for this oxidation product. It

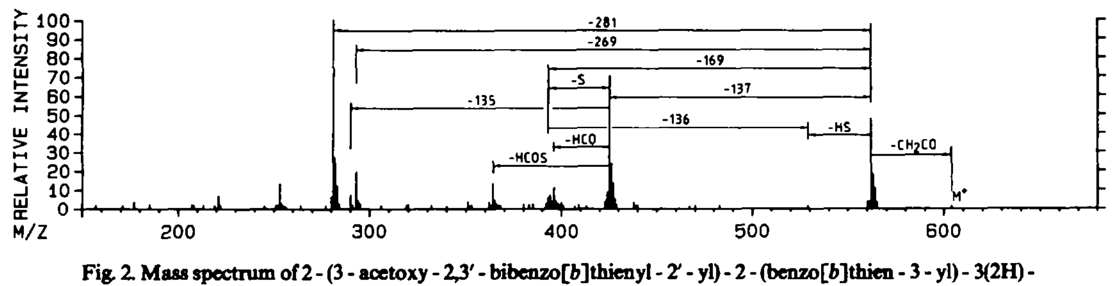


Fig. 2. Mass spectrum of 2 - (3 - acetoxy - 2,3′ - bibenzo[*b*]thienyl - 2′ - yl) - 2 - (benzo[*b*]thien - 3 - yl) - 3(2H) - benzo[*b*]thiophenone (**11b**), *m*/*z* > 150 daltons, only peaks > 1.4% of base peak.

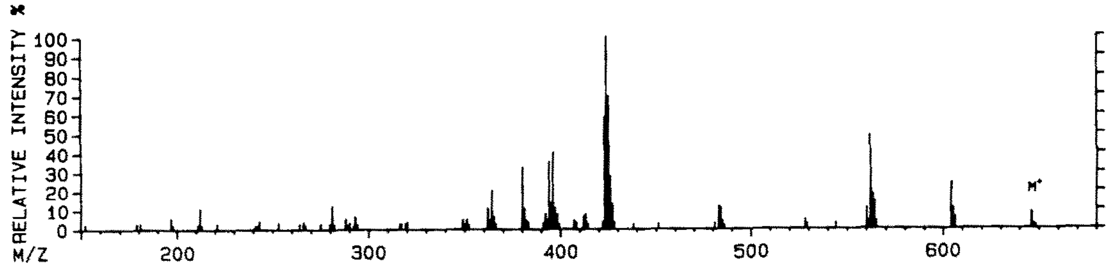


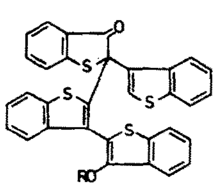
Fig. 3. Mass spectrum of 3,3‴ - diacetoxy - 2,3′:2′,2″:3″,2‴ - quaterbenzo[*b*]thiophene (**12b**), $m/z > 150$ daltons, only peaks $> 1.9\%$ of base peak.

follows then that either **11a** or **12a** might be an intermediate in a complex reaction. This proposal is strengthened by the fact that 3-hydroxy-2,2′-biindolyl (**17**) in basic solution, upon aeration gives[11] a dimeric oxidative coupling product analogous to **23** (the structure was corroborated by an independent synthesis). A compound analogous to **12a** was proposed as an intermediate (not isolated).

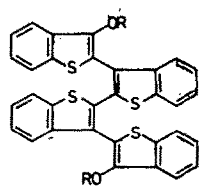
Therefore, we treated **11a** and **12a** with potassium ferricyanide–potassium hydroxide in dioxane–water. Compound **11a** gave a product identical with compound C. Thus, if structure **11a** is correct, the oxidation product, C, must have structure **20**. The product obtained from the oxidation of **12a** also had a molecular ion at *m*/*z* 560. However, there were some differences in the mass spectrum (Fig. 5) as well as in the IR spectrum as compared with the spectra of compound C. This compound must then have the structure **23**.

Compounds **20** and **23** have the possibility of *cis* and *trans* arrangements of the two 3(2H)-benzo[*b*]-thiophenone systems, but no indications of the presence of different stereoisomers were obtained. These compounds are difficult to dissolve in common solvents. Therefore, no attempts have been made to get information about the stereochemistry and no simple means seems obvious for such a study.

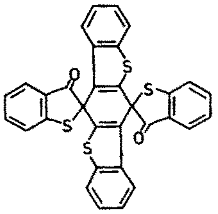
Compound **20** has in fact already been prepared, but not characterized, by Krollpfeiffer.[6] In connection with the chemical characterization of 3-hydroxy-2,3′-bibenzo[*b*]thienyl he reports: "Aus der wässrig alkalischen Lösung fällt Ferricyankalium in der Kälte einem gelbbraunen Niederschlag." That compound must be identical with our **20**.



11 a R=H
b $R=COCH_3$



12 a R=H
b $R=COCH_3$



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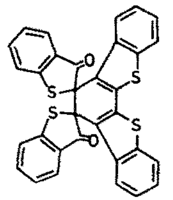

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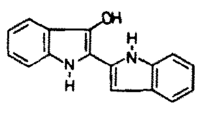

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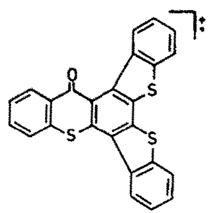

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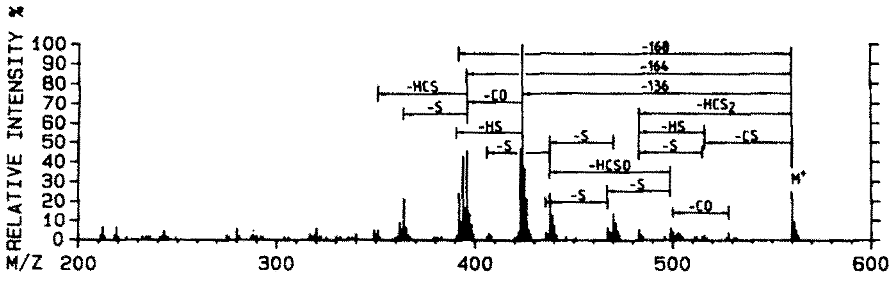


Fig. 4. Mass spectrum of dispiro[6,12 - dihydro - bis(benzo[*b*]thieno)[2,3-*a*:2′,3′-*d*]benzene - 6,2′:12,2″ - bis-(3(2H) - benzo[*b*]thiophenone)] (**20**), $m/z > 200$ daltons, only peaks $> 1.2\%$ of base peak.

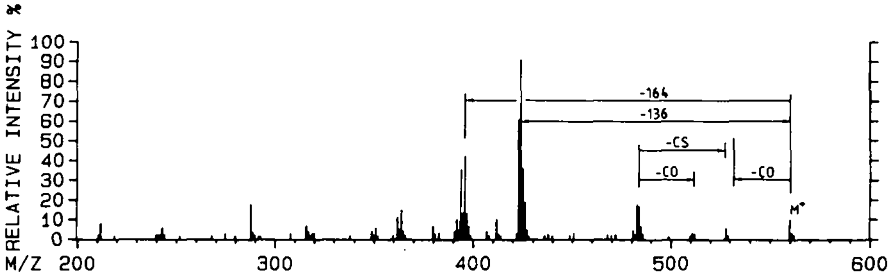
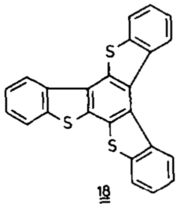


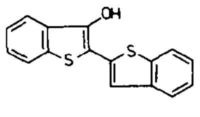
Fig. 5. Mass spectrum of dispiro[6,7 - dihydro - bis(benzo[*b*]thieno)[3,2-*a* : 2′,3′-*c*]benzene - 6,2′ : 7,2″ - bis(3(2H) - benzo[*b*]thiophenone)] (**23**), *m*/*z* >200 daltons, only peaks >1.5% of base peak.

*Experiments in mono- and dichloroacetic acid*

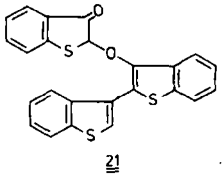
Re-examination of the experiments performed by Dalgliesh and Mann[7] was made in order to firmly establish the cyclotrimeric structure as well as to explain their "bimolecular associate" of **8a**. In our hands, treatment of 3(2H)-benzo[*b*]thiophenone with dichloroacetic acid at 170° gave a solid, which was extracted with ethanol and dichloromethane. This left tris(benzo[*b*]thieno)[2,3 : 2′,3′ : 2″,3″]benzene (**9**). The dichloromethane extract was evaporated, which gave a compound with an IR spectrum clearly different from that of the trimer **9** and with a considerably lower m.p. (253–255°). However, the mass spectrum showed a molecular ion at *m*/*z* 396 and was very similar to that of the trimer **9**. We therefore considered this compound to be the isomeric trimer **18**. Its formation can be explained by assuming an acid-induced isomerization of the initially formed dimer **8a** to 3-hydroxy-2,2′-bibenzo[*b*]thienyl (**19**), analogous to what happens to a much greater extent in the cyclocondensation of N-methyl-3(2H)-indolone.[4] Benzo[*b*]thiophenes which are aryl-substituted in the 3-position, have been reported[14,29] to undergo acid-catalyzed isomerization to the 2-isomer. TLC of the ethanol-soluble material showed several spots, but no one dominated. The oxepin **10** was absent in the mixture, and the presence or absence of the dimer **8a** could not be established from the TLC. However, treating 3-hydroxy-2,3′-bibenzo[*b*]thienyl with dichloroacetic acid at 170° left no remaining starting material.



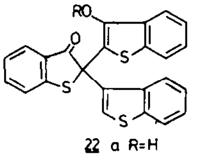
**18**



**19**



**21**



**22** a R=H
b R=COCH3

Treatment of 3(2H)-benzo[*b*]thiophenone with dichloroacetic acid at a somewhat lower temperature (125°) gave a different product pattern. The yield of the cyclotrimer **9** was decreased to only 1% and the unsymmetrical cyclotrimer **18** was not found. The cyclotrimer was instead accompanied by the oxepin **10**. From the material soluble in ethanol, the 2,2′-coupling product (**11a**) of 3-hydroxy-2,3′-bibenzo[*b*]thienyl was isolated. The remaining ethanol-soluble material was complex, giving several spots on the TLC. An intense spot having the same $R_f$-value as 3-hydroxy-2,3′-bibenzo[*b*]thienyl (**8a**) was present.

When the condensation medium was monochloroacetic acid at 180°, the solid material consisted of the cyclotrimer **9**, the unsymmetrical cyclotrimer **18**, and the oxepin **10**. Furthermore, from material soluble in ethanol we could isolate the oxidation product **20**. However, due to the low solubility of the compound in ethanol, we have doubts about its presence in the original mixture. Instead, it might have been formed from **11a** during work up. The oxepin **10** decomposes when treated with dichloroacetic acid at 170°, which explains the absence of this product in the condensation performed under these conditions. Thus, we believe that the compound Dalgliesh and Mann[7] assigned to be the "bimolecular associate" of **8a** was in fact the 2,2′-coupling product **11a** or the product of further oxidation, **20**.

*Experiments with bromine in carbon disulfide*

In connection with this study we observed that Krollpfeiffer[6] had suggested structure **21** for a compound obtained when treating 3(2H)-benzo[*b*]thiophenone (3 mol) with bromine (1 mol) in carbon disulfide. The reaction was thought to proceed via formation of 2-bromo-3(2H)-benzo[*b*]thiophenone and 3-hydroxy-2,3′-bibenzo[*b*]thienyl (HBr is formed in the bromination reaction, and will then catalyze the condensation). The product could also be obtained by mixing the proposed intermediates. However, we considered the formation of an ether of this type (**21**) highly unlikely under the conditions used. Repetition of Krollpfeiffer's experiment yielded a compound with both an OH and a CO group (IR : $\nu_{OH} = 3215\ cm^{-1}$ and $\nu_{CO} = 1665\ cm^{-1}$). The compound gave a molecular ion at *m*/*z* 430. Acetylation led to a monoacetate (Fig. 6), with the CO function still in the molecule. Analysis by $^{13}C$-NMR spectroscopy of the parent compound showed, besides the resonances in the aromatic region, a downfield singlet at 198.22 ppm and an upfield singlet at 63.82 ppm. The downfield singlet is probably caused by a CO

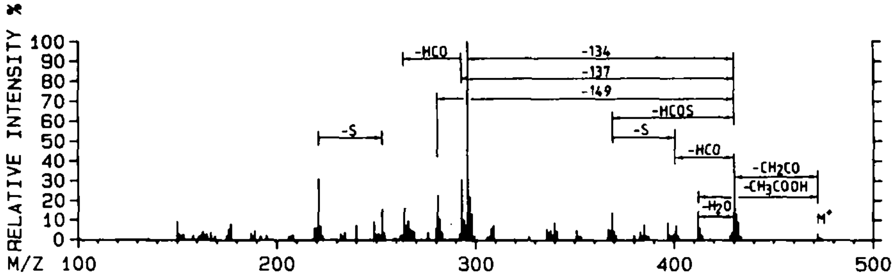


Fig. 6. Mass spectrum of 2 - (3 - acetoxybenzo[*b*]thien - 2 - yl) - 2 - (benzo[*b*]thien - 3 - yl) - 3(2H) - benzo[*b*]thiophenone (**22b**), $m/z > 150$ daltons, only peaks > 1.7% of base peak.

carbon, e.g. the ketonic carbon in a 3(2H)-benzo[*b*]thiophenone-ring system. In fact, 3(2H)-benzo[*b*]thiophenone itself exhibits a CO carbon resonance at 199.8 ppm.[15] The upfield singlet is indicative of a fully substituted $sp^3$ carbon. These facts show that the compound cannot have the structure (**21**) assigned by Krollpfeiffer. However, the data are in consonance with the isomeric structure **22a**. The compound can be considered as an unsymmetrical oxidative coupling product of 3(2H)-benzo[*b*]thiophenone and 3-hydroxy-2,3'-bibenzo[*b*]thienyl (reacting at the 2-carbon), catalyzed by bromination of the 2-position in 3(2H)-benzo[*b*]thiophenone. It is noteworthy that the previously discussed oxepin **10** is thought to be formed via an oxidative coupling, but with coupling to the 2'-carbon in the dimer **8a** (Scheme 3). In that case, the initially formed product would have the possibility of undergoing a ring closure, which could lead to the end product. The oxepin **10** was also present in small amounts in the mixture when **22a** was formed (TLC).

## DISCUSSION OF MASS SPECTRA

Some of the compounds obtained were studied by linked scanning mass spectrometry to get information about fragmentation pathways.[26] Daughter ions of a particular precursor ion are measured by scanning the magnetic (*B*) and the electrostatic (*E*) sector such that the ratio $B/E$ is maintained constant. In this way only ions formed from the selected ion in the first field free region are transmitted. By scanning the magnetic and electrostatic fields simultaneously such that the ratio $B^2/E$ is maintained constant, it is possible to study the precursor ions leading to a particular daughter ion. In Figs 1–7 a daughter ion determination is indicated by a left-hand arrow, and a right-hand arrow indicates a parent ion determination.

The mass spectrum of tris(benzo[*b*]thieno)[3,2-*b*:2',3'-*d*:2'',3''-*f*]oxepin (**10**) is shown in Fig. 1. The molecular ion is predominant and the stability of the molecule is demonstrated by the doubly and even triply charged ions. In fact, most of the fragments formed also appear in the doubly charged form. The relatively sparse fragmentation is explained by elimination of O, HCO, S, CS, HCS and HCOS from the molecular ion. The ions formed eliminate further HCO, S, HCS as indicated in Fig. 1. The compositions of the ions at $m/z$ 412, 396, 380 and 351 were confirmed with high-resolution mass spectrometry. Elimination of S, CS and HCS from benzo[*b*]thiophene systems, e.g. dibenzothiophene, has been reported.[25] The oxygen expulsion is a very rare fragmentation. It parallels the reported[19] elimination of oxygen from dibenzo-1,4-dioxin. However, this elimination from dibenzo-1,4-dioxin is not mentioned in another fragmentation study,[20] and there is no ion corresponding to $[M-16]^+$ in the reported[22] mass spectrum of tribenz[*b,d,f*]oxepin (**26**). The interpretation of the daughter ion spectrum is complicated by the fact that an elimination of 17 is much more abundant than the elimination of 16. However, it is very unlikely that 17 could be anything but OH and 16 anything but O in this case. Thus, we interpret the results to show that loss of O gives rise to a very stable ion, with very little further fragmentation. The OH loss must give rise to an unstable ion, since the peak at $m/z$ 395 is fully explained as the $^{13}C$ isotope peak of $m/z$ 394. However, the presence of an ion at $m/z$ 395 formed from $m/z$ 412 in the first field free region was clearly shown in the parent ion determination.

During the mass spectrometric studies, we found **8a**, **11a**, **12a** and **22a** to be difficult to handle due to their instability, especially at the high probe temperature necessary for the three latter compounds. The acetates (**8b**, **11b**, **12b** and **22b**) were much simpler to handle and gave reproducible mass spectra, and were therefore used in the fragmentation studies. The acetates eliminate ketene until the parent compound is obtained. No other impacts have been assumed on the fragmentation.

3 - Acetoxy - 2,3' - bibenzo[*b*]thiophene (**8b**) was studied as a model. The spectrum and the interpretation of the main fragment ions are shown in Fig. 7. The experiment shows that HCO is lost both in a single step as well as a stepwise loss of CO followed by H. The elimination of HCS also occurs stepwise as well as in a single step.[25] The structure of **22b** (assigned to be 2 - (3 - acetoxybenzo[*b*]thien - 2 - yl) - 2 (benzo[*b*]thien - 3 - yl) - 3(2H) - benzo[*b*]thiophenone), is strongly supported by the fragmentation pattern. The base peak at $m/z$ 296 (Fig. 6), is explained by a 1,4-elimination of benzo[*b*]thiophene (134 daltons) from the parent ion at $m/z$ 430 forming the radical ion of $[\Delta^{2,2'}$-(3H,3H')-bibenzo[*b*]thiophene]-3,3'-dione (thioindigo). Thioindigo itself shows a very sparse fragmentation.[27] The loss of 149 daltons is explained by loss of the 3-hydroxybenzo[*b*]thien-2-yl group and the species formed ($m/z$ 281) should undergo the same fragmentation as **8b**, which also seems to be the case ($m/z$ 281 → $m/z$ 253 → $m/z$ 221 → $m/z$ 177). The elimination of 137 daltons is not structurally obvious, but we conclude that this is elimination of the 3-

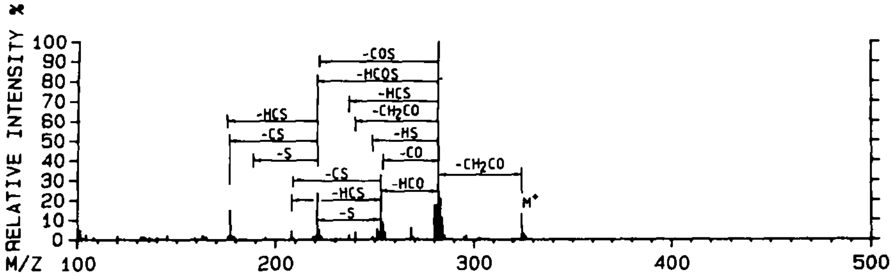


Fig. 7. Mass spectrum of 3-acetoxy-2,3′-bibenzo[*b*]thienyl (**8b**), *m*/*z* > 100 daltons, only peaks > 0.9% of base peak.

hydroxybenzo[*b*]thien-2-yl moiety with the exception of the 2-carbon. The ion at *m*/*z* 293 is probably a rearrangement ion.

If the structures assumed for the 2,2′-coupled **11a** and **b** are correct, then they represent benzo[*b*]thiophene homologues of **22a** and **b**. This structural similarity is strongly supported by the mass spectrometric data (Fig. 2). Compound **11b** shows the elimination of a fragment of 137 daltons (as **22b**) as well as an elimination of a benzo[*b*]thiophene-homologous fragment (269 daltons). In the same way, the loss of 281 daltons corresponds to the loss of 149 daltons from **22b**.

The mass spectrum of the 2′,2′-coupled **12b** (Fig. 3) is to a large extent explained by a dehydrogenation (*m*/*z* 562 → *m*/*z* 560). When the mass spectrum of **23** (the oxidation product of **12a**) is subtracted from that of **12b**, most of the peaks are eliminated. The ions at *m*/*z* 425 and *m*/*z* 380 remain strong, and the loss of 137 daltons is probably explained for this structure as for the two latter structures discussed. The pathway seems in this case to be less favourable. The fragmentations leading to *m*/*z* 293 and especially *m*/*z* 281 are not common for this structure.

The mass spectrum of the final oxidation products **20** (Fig. 4) and **23** (Fig. 5) are both dominated by the ion clusters around *m*/*z* 424 and *m*/*z* 396. The daughter ion recordings of the molecular ions (*m*/*z* 560) show a clear difference in the important pathways for their fragmentations. For **20** the molecular ion fragments to *m*/*z* 516, *m*/*z* 483 (minor), *m*/*z* 424 (predominant), *m*/*z* 396 and *m*/*z* 392. The fragmentation of the isomeric **23** is totally dominated by formation of *m*/*z* 424, but with a contribution of *m*/*z* 532 and *m*/*z* 396 (very minor). We have tentatively assigned structure **28** for the radical ion at *m*/*z* 424. The formation of this ion from a framework of structure **23** seems explainable. It is also understandable that a framework of structure **20** will have relatively more difficulties to fragment and rearrange to form an ion of structure **28** (if the ion at *m*/*z* 424 is the same for both compounds) and this increases the importance of other pathways.

## CONCLUSIONS

This study has shown that cyclocondensation products are obtained from 3(2H)-benzo[*b*]thiophenone in the reaction media used. Compared to the cyclocondensation of 3(2H)-benzo[*b*]furanone,[2,12] not only the symmetrical cyclotrimer **9** is formed, but also the unsymmetrical cyclotrimer **18**. However, the unsymmetrical cyclotrimer was only found in reactions performed at high temperatures (170–180°). The dimeric condensation product, 3-hydroxy-2,3′-bibenzo[*b*]thienyl (**8a**), formed in the first step towards the cyclotrimers is very prone to undergo oxidative coupling reactions. We have isolated compounds that seem to be formed by 2,2′- as well as 2′,2′-coupling of two molecules of 3-hydroxy-2,3′-bibenzo[*b*]thienyl (**11a** and **12a**). These compounds can be further oxidized to **20** and **23**. 3-Hydroxy-2,3′-bibenzo[*b*]thienyl can also couple to 3(2H)-benzo[*b*]thiophenone. We conclude that tris(benzo[*b*]thieno)[3,2-*b*:2′,3′-*d*:2″,3″-*f*]oxepin (**10**) is formed via a coupling of the 2-carbon in 3(2H)-benzo[*b*]thiophenone to the 2′-position (Scheme 3) and the product arising from coupling to the 2-position is also reported in this paper. These results show that 3-hydroxy-2,3′-bibenzo[*b*]thienyl has properties very typical for a phenol.

## EXPERIMENTAL

M.ps were determined on a micro hot stage apparatus and are uncorrected. TLC was run on $SiO_2$ 60 $F_{254}$ (Merck) in $CH_2Cl_2$ (unless otherwise stated) and column chromatography was done on $SiO_2$ 60, 0.063–0.200 mm (Merck). IR spectra were recorded with a Perkin–Elmer 257 IR spectrophotometer, being determined on KBr discs. $^{13}C$-NMR spectra were obtained using a Bruker WP 200 spectrometer. Mass spectra (EI, 70 eV) were obtained with a VG 7070E double focusing instrument operated at 6 kV accelerating voltage. The direct probe was used and the ion source was kept at 250–350°, depending on the probe temp necessary to give good recording conditions. The resolution was *ca* 1000 and the spectra were recorded on an oscillographic recorder. GC/MS analyses were carried out with a 15 m × 0.3 mm fused silica capillary column coated with SE-52 (column temp: 250°), directly connected to the ion source. Only major peaks and peaks of diagnostic value are listed. The daughter and parent ions are listed as "daughters" and "parents", usually without reporting their relative abundance. High-resolution mass determinations were done on a Varian MAT 711 instrument.

3(2H)-Benzo[*b*]thiophenone (**7**) was prepared[28] from (2-carboxyphenylthio)acetic acid under strong alkaline conditions. The compound was recrystallized from petroleum ether (b.p. 40–60°) and dried *in vacuo* immediately before use. We found this route fast and convenient, although other methods exist (cf. Ref. 30). Precautions have to be taken for storage of 3(2H)-benzo[*b*]thiophenone, since the compound is readily oxidized to coloured products.

Acetylations were performed by treating the substrate (100 mg) with $Ac_2O$ (5.0 ml) containing pyridine (0.5 ml) at reflux for 2 hr. The mixture was poured into water and the solid material was collected and purified. If solid material was not obtained, the soln was neutralized with $NaHCO_3$, extracted with $CH_2Cl_2$, dried ($Na_2SO_4$) and evaporated.

### *Treatment of* 3(2H)-*benzo*[*b*]*thiophenone with* HCl *in* HOAc

These reactions were performed in a heavy-walled glass tube (25 mm OD) with a screwcap having a PTFE-washer (total volume *ca* 50 ml).

(1) 3(2H)-Benzo[*b*]thiophenone (2.50 g, 17 mmol) in HOAc (25 ml) saturated with HCl was heated to 100° with stirring for 8 hr. Solid material started to precipitate after *ca* 10 min. The reaction vessel was found to be leakfree since no HCl was detected with pH-paper during the heating. The mixture was allowed to cool to room temp and the slightly yellow solid material formed was collected and washed with a few ml of HOAc, whereupon the solid was carefully extracted with $CH_2Cl_2$. This treatment left a pale rose coloured solid of **9**, yield 52 mg (2.4%), m.p. > 360° (lit.[7,9] m.p. 422–425° and 422°, respectively). The analytical sample was recrystallized from xylene. IR: 1560, 1545, 1460, 1442, 1352, 1310, 1265, 1190, 1158, 1022, 889, 770, 718, 703 cm$^{-1}$. MS: 396 ($M^+$, 100), 394 (8), 198 ($M^{2+}$, 17), 132 ($M^{3+}$, 0.9). The $CH_2Cl_2$ extract was evaporated and the residue was recrystallized from $CH_3CN$, yield 25 mg (1.1%) of yellow **10**, m.p. 252–254°. The analytical sample was obtained after column chromatography with $CH_2Cl_2$ as eluent. Although the compound is sparingly soluble in $CH_2Cl_2$ and therefore tails, this was the method that gave the purest material. (Found: C, 69.6; H, 3.0; S, 23.4. Calc for $C_{24}H_{12}OS_3$: C, 69.87; H, 2.94; S, 23.31%.) IR: 1437, 1421, 1360, 1347, 1320, 1312, 1144, 1094, 1022, 752, 745, 719, 669, 666 cm$^{-1}$. MS: 412 ($M^+$, 100), 396 (15), 383 (21), 380 (34), 351 (17), 206 ($M^{2+}$, 11), 137.3 ($M^{3+}$, 0.5) and Fig. 1. Daughters: 412 → 396, 395, 383, 380, 368, 367, 351; 396 → 364, 351; 383 → 351, 338; 380 → 351; 351 → 319, 306. Parents: 351 → 380, 383, 412; 380 → 412; 383 → 412; 395 → 412; 396 → 412. High-resolution MS: 412.0060 (0.0010) $C_{24}H_{12}OS_3$, 396.0053 (−0.0048) $C_{24}H_{12}S_3$, 380.0346 (0.0016) $C_{24}H_{12}OS_2$, and 351.0352 (0.0050) $C_{23}H_{11}S_2$.

The HOAc filtrate was poured into water (*ca* 100 ml) and was left overnight. The ppt was collected and treated with toluene and 2,2,4-trimethylpentane. This afforded 810 mg (34%) of crude **8a** (TLC: $R_f = 0.59$), *vide infra*. The toluene–2,2,4-trimethylpentane soln was taken to dryness and treated with $CH_3CN$, which gave two crops of solid material. The first crop (126 mg) contained mainly a compound A (TLC: $R_f = 0.75$) and the second (134 mg) contained mainly two compounds, A (TLC: as above) and B (TLC: $R_f = 0.41$). The analytical sample of compound A was obtained after several recrystallizations from $CH_3CN$. The compound could also be purified by column chromatography with $CH_2Cl_2$–hexane (1 : 1) as eluent. By extracting a mixture containing compound B with acetone and then treating the undissolved material with $CH_3CN$, a rather pure material was obtained which has been used in the characterization. Compound B is not stable enough for column chromatography on $SiO_2$. An aliquot (75 mg) of the mixture of compounds A and B was acetylated using the general procedure, yielding 84 mg of crude product. This material was subjected to column chromatography with a mixture of toluene–heptane–diisopropyl ether (5:4:1) as eluent. The material was separated into 34 mg of a compound later shown to be the acetate of compound A, 15 mg of a mixture of both compounds and finally 29 mg of a compound later shown to be the acetate of compound B (93% of applied material recovered). Compound A is **11a**: yellow crystals, m.p. 198–200° ($CH_3CN$). IR: 3290 (OH), 1680 (C=O), 1588, 1508, 1450, 1441, 1431, 1340, 1315, 1287, 1266, 1253, 1220, 1168, 1080, 1035, 1020, 935, 763, 756, 748, 732, 652, 628 cm$^{-1}$. $^{13}$C-NMR ($CDCl_3$): 200.75, 67.25. The aromatic carbon atoms resonated between 152.36 and 121.02. MS: 562 ($M^+$). The MS was much disturbed by the oxidation product **20** formed in the instrument. The acetate is **11b**: white crystals, m.p. 137–142° (ether–hexane). Attempts to further purify this material failed, presumably due to further oxidation. IR: 1770 (C=O), 1695 (C=O), 1580, 1448, 1439, 1428, 1350, 1288, 1190, 1042, 758, 730 cm$^{-1}$. MS: 604 ($M^+$, 2), 562 ($[M-42]^+$, 48), 425 (70), 281 (100) and Fig. 2. Daughters: 562 → 529, 425, 393, 293, 281; 425 → 396, 393, 364, 290. Parents: 281 → 562; 293 → 562; 393 → 425, 529, 562; 425 → 562; 562 → 604.

Compound B is **12a**: yellow crystals, m.p. 189–192° ($CH_3CN$), impurities still present. IR: 3420 (OH, br), 1587, 1460, 1442, 1425, 1408, 1378, 1365, 1351, 1320, 1281, 1261, 1229, 1176, 1166, 1083, 1045, 1020, 760, 740 cm$^{-1}$. MS: 562 ($M^+$). The MS was much disturbed by the oxidation product **23** formed in the instrument. The acetate is **12b**: white crystals, m.p. 266–268° (column chromatography with $CH_2Cl_2$–hexane (3 : 1) as eluent, crystallized from EtOH). IR: 1770 (C=O), 1436, 1354, 1317, 1187, 1165, 1155, 1149, 1132, 1080, 1050, 1015, 879, 764, 750, 740, 731, 726 cm$^{-1}$. MS: 646 ($M^+$, 9), 604 ($[M-42]^+$, 24), 562 ($[M-42-42]^+$, 49), 425 (70), 424 (100), 396 (40), 394 (35), 380 (33) and Fig. 3. The following doubly charged ions are excluded from the figure: 212.5 (4), 211.5 (12), 195.5 (2) and 174.5 (3). The acetates formed from purified **11a** and **12a** were in all respects identical with the acetates obtained from the mixture.

(2) The condensation reaction was repeated with 3(2H)-benzo[*b*]thiophenone (1.00 g, 6.7 mmol) in HOAc (10 ml) saturated with HCl, which was left in the sealed tube for 48 hr. Small amounts of solid material was filtered off and discarded. The HOAc filtrate was poured into water (*ca* 100 ml) and left overnight. The ppt formed was collected, yield 0.80 g (85%) of light brown **8a** (TLC: $R_f = 0.59$), *vide infra*.

### *Treatment of* 3(2H)-*benzo*[*b*]*thiophenone with* HCl *in* $CHCl_3$ (cf. *Refs* 5 *and* 6)

(1) 3(2H)-Benzo[*b*]thiophenone (4.00 g, 27 mmol) was dissolved in dry $CHCl_3$ (40 ml). HCl (passed through conc $H_2SO_4$) was introduced into the stirred soln, first at 0° (20 min) and then at 25° (40 min) with exclusion of the air. Excess HCl was then removed with $N_2$, and the soln was left overnight. Compound **8a** was collected, yield 0.50 g (13%), m.p. 133–136° (lit.[5,6] m.p. 129.5–130° and 132–133°, respectively). IR: 3510 (OH, sharp), 1592, 1588, 1493, 1436, 1420, 1408, 1348, 1227, 1131, 1075, 1050, 1015, 862, 859, 795, 763, 754, 739, 730 cm$^{-1}$. MS: 282 ($M^+$, 100), 253 (58), 221 (24), 177 (20).

The acetate **8b** was prepared by treatment with $Ac_2O$–NaOAc,[5] in 81% yield (EtOH, charcoal), m.p. 131–133° (lit.[5] m.p. 133.5°). IR: 1765 (C=O), 1575, 1434, 1418, 1363, 1350, 1334, 1196, 1183, 1155, 1138, 1129, 1077, 1055, 1042, 1015, 874, 849, 781, 767, 755, 741, 739, 713 cm$^{-1}$. MS: 324 ($M^+$, 13), 282 ($[M-42]^+$, 100), 253 (33), 221 (24), 177 (15) and Fig. 7. Daughters: 324 → 282; 282 → 254, 253, 249, 240, 237, 222, 221; 280 → 252, 236; 254 → 221, 210, 209; 253 → 221, 209, 208; 221 → 189, 177, 176. Parents: 221 → 253, 254; 253 → 282; 254 → 282; 282 → 324.

(2) The reaction was repeated, but with less efficient exclusion of the air. The mixture was left with stirring overnight, then diluted with $CHCl_3$ (50 ml), water (100 ml) was added and the mixture was neutralized with $NaHCO_3$. The $CHCl_3$ phase was collected, washed with water, dried ($Na_2SO_4$) and evaporated. Crystallization of the residue from $CH_3CN$ gave 430 mg (11%) of **11a**.

### *Treatment of* 3(2H)-*benzo*[*b*]*thiophenone with dichloroacetic acid*

(1) 3(2H)-Benzo[*b*]thiophenone (1.50 g, 10 mmol) and dichloroacetic acid (12 ml) were mixed and heated to 170° with stirring for 1 hr. The mixture was set aside overnight, then poured into water (*ca* 100 ml) and left for another night. The solid material was collected and extracted with boiling EtOH (100 ml) for 10 min. The EtOH was decanted off, and the extraction was repeated once. The residual solid material was further extracted with portions of refluxing $CH_2Cl_2$ (total 80 ml or until no material moving on TLC could be detected). This yielded **9** (678 mg, 51%) with IR and MS as before. The $CH_2Cl_2$ extract was evaporated, and after treatment with hot $CH_3CN$, white crystals of **18** (98 mg, 7.4%), m.p. 253–255°. IR: 1455, 1432, 1334, 1315, 1232, 1182, 1152, 1030, 752, 743, 719, 705 cm$^{-1}$. MS: 396 ($M^+$, 100), 394 ($[M-2]^+$, 31), 364 (6), 198 ($M^{2+}$, 10), 197 ($[M-2]^{2+}$, 13), 132 ($M^{3+}$, 0.3). TLC: $R_f =$

0.82. (This $R_f$-value is also obtained from the oxepin **10** and we have not found any system that separates them. However, they differ in the fluorescence at 365 nm, this compound having blue fluorescence, and the oxepin has yellow fluorescence as well as being yellow in visible light.)

The EtOH-soluble material was examined by TLC which revealed several spots without any one dominating. No spot corresponding to the oxepin **10** ($R_f$ = 0.82, yellow) was present. The presence of **8a** could not be established (cf. Ref. 7). All attempts to get purified material from this mixture failed.

(2) 3(2H)-Benzo[*b*]thiophenone (920 mg, 6.1 mmol) and dichloroacetic acid (8 ml) were mixed and heated to 125° with stirring for 1 hr. The mixture was treated as under (1). This yielded **9** (11 mg, 1.4%). The material extracted by $CH_2Cl_2$ was in this experiment **10** (65 mg, 7.7%) and we found no trace of **18**. The EtOH-soluble material was evaporated, redissolved in hot $CH_3CN$, filtered while still hot, and after cooling, crystals of **11a** (68 mg, 7.9%) were obtained. The remaining material was examined by TLC, which revealed several spots. However, a spot with $R_f$ = 0.59 was present, the same $R_f$-value as for **8a**.

### *Treatment of* 3(2H)-*benzo*[*b*]*thiophenone with monochloroacetic acid*

3(2H)-Benzo[*b*]thiophenone (1.50 g, 10 mmol) and monochloroacetic acid (15 g) were mixed and heated to 180° with stirring for 1 hr. The mixture was treated with water and EtOH as described for the experiments in dichloroacetic acid. The residual solid material was extracted with refluxing $CH_3CN$ (*ca* 400 ml), which left a mixture of the trimers **9** and **18** (76 mg) as indicated by TLC and IR. The mixture was extracted carefully with refluxing $CH_2Cl_2$, and pure **9** (48 mg, 3.6%) was obtained. The $CH_2Cl_2$ extract was evaporated which yielded **18** (9.4 mg, 0.7%) after recrystallization from $CH_3CN$. The $CH_3CN$ extract gave after evaporation to *ca* 100 ml, **10** (120 mg, 8.7%). This material might contain small amounts of the trimer **18** (IR, TLC). The EtOH extract was evaporated and treated with $CH_3CN$. A brownish material was obtained (193 mg). In further efforts to purify this material, it was treated with acetone, which gave a light brown material, later shown to be **20** (130 mg, 9.3%). All further attempts to get purified material from the EtOH extract failed.

### *Treatment of 3-hydroxy-2,3'-bibenzo[b]thienyl with dichloroacetic acid*

Compound **8a** (390 mg, 1.4 mmol) and dichloroacetic acid (3 ml) were mixed and heated to 170° for 1 hr. The mixture was treated with water and EtOH as previously described. No starting material remained (TLC). The product pattern was complex.

### *Treatment of tris(benzo[b]thieno)*[3,2 - *b*: 2',3' - *d*: 2",3" - *f*]-*oxepin with dichloroacetic acid*

Compound **10** (200 mg, 0.49 mmol) and dichloroacetic acid (3 ml) were mixed and heated to 170° for 3 hr. The mixture was treated with water and the solid material formed was examined by TLC. Several strong spots were detected in the small amount of material that was dissolved. The starting material ($R_f$ = 0.82, yellow) was present, but in very minute amounts.

### *Reductive desulfurization with Raney* Ni

The substrate (200 mg) and Raney Ni (*ca* 9 g) were refluxed in dry dioxane (25 ml) for 6 hr, and the hot soln was filtered and the Raney Ni was further washed with hot dioxane (3 × 25 ml). The combined dioxane phases were evaporated, redissolved in $CH_2Cl_2$, dried ($Na_2SO_4$) and evaporated. The residues were subjected to column chromatography with $CH_2Cl_2$–hexane (3 : 1) as eluent.

Treatment of **9** with Raney Ni yielded 59 mg (38%) of 1,3,5-triphenylbenzene. MS: 306 ($M^+$, 100), 289 (7), 276 (2), 228 (5), 226 (5), 202 (2), 153 ($M^{2+}$, 2). The compound was compared with independently synthesized 1,3,5-triphenylbenzene[13] and they were shown to be identical by GC/MS.

Treatment of **10** with Raney Ni yielded 110 mg (71%) of **24** as an oil. MS: 314 ($M^+$, 51), 210 (22), 131 (37), 117 (27), 105 (16), 104 (14), 91 (100). This compound was compared with independently synthesized 1,3,6-triphenylhexane, *vide infra*, and they were shown to be identical.

### *Independent syntheses of* 1,3,6-*triphenylhexane*

*Method A.* 1,3-Diphenylpropan-1-one (dihydrobenzylideneacetophenone) (6.30 g, 30 mmol) was added to a soln prepared from 1-bromo-3-phenylpropane (6.70 g, 34 mmol) and Mg (0.85 g, 35 meq) in dry ether (150 ml). After completion of the reaction (3 hr at reflux temp) the mixture was cooled and treated with $NH_4Cl$ (aq, 10%, 100 ml). The ether phase was collected, washed with water, dried ($Na_2SO_4$) and evaporated. Crystallization of the residue from diisopropyl ether–hexane gave **25** (7.10 g, 72%), m.p. 65–66°. IR: 3570 (OH), 3450 (OH, br), 3083, 3058, 3020, 2938, 2855, 1602, 1496, 1453, 1447, 1065 (br), 1030, 913, 766, 749, 701 $cm^{-1}$. $^{13}C$-NMR ($CDCl_3$): 74.99 (s), 44.58 (t), 42.44 (t), 35.52 (t), 29.51 (t), 25.27 (t). The aromatic C atoms resonated between 146.76 and 125.29.

1,3,6-Triphenyl-3-hexanol (1.65 g, 5.0 mmol) was dissolved in dry THF (15 ml) and pyridine–$SO_3$ complex (10 mmol) was added with stirring at 0°. After 12 hr at 0° $LiAlH_4$ (1.14 g, 30 mmol) was added and the stirring was continued for 1 hr at 0°, whereupon the temp was allowed to rise to 25° and then the mixture was stirred at this temp for 5 hr. Excess $LiAlH_4$ was destroyed by addition of NaOH (aq, 2%, 20 ml). The product was then partitioned between ether and water. The organic extract was washed with water, dried ($MgSO_4$), evaporated and distilled (b.p. 110–115°, 0.1 mmHg) to yield 1.33 g (85%) **24** as a oil. IR: 3082, 3060, 3022, 2926, 2855, 1603, 1496, 1454, 1073 (br), 1032, 912, 755, 738, 702 $cm^{-1}$. $^{13}C$-NMR ($CDCl_3$): 45.52 (d), 38.51 (t), 36.58 (t), 35.96 (t), 33.86 (t), 29.22 (t). The aromatic C atoms resonated between 145.49 and 125.20. MS: 314 ($M^+$).

*Method B.* 3-Phenylpropyllithium was generated *in situ* from 1-bromo-3-phenylpropane (6.70 g, 34 mmol) and Li foil (0.24 g, 35 meq) in dry ether (100 ml). 1,3-Diphenylpropen-3-one (benzylideneacetophenone) (6.24 g, 30 mmol) in dry ether (30 ml) was then added at 25°. After 2 hr at this temp, the mixture was cooled (to −25°) and ammonia (*ca* 150 ml) was distilled into the mixture, whereupon Li wire (0.69 g, 100 meq) was added in portions. When the Li wire had been consumed, the dark-blue mixture was stirred for 1 hr, whereupon $NH_4Cl$ (15.0 g) was carefully added. After completed addition, the ammonia was allowed to evaporate from the now light-yellow mixture. After partition of the residue between brine and ether, the organic phase was dried ($MgSO_4$), evaporated and distilled (b.p. 110–115°, 0.1 mm Hg) to yield an oil (7.54 g, 80%), which was identical in all respects with **24** obtained by using method A.

### *Oxidations with potassium ferricyanide*

Compound **8a** (0.20 g, 0.71 mmol) was dissolved in dioxane (5 ml). $K_3[Fe(CN)_6]$ (0.30 g) and KOH (0.30 g) in water (10 ml) were added. The mixture was refluxed for 5 min. After cooling the mixture, the solid formed was collected. Quantitative yield of **20**, m.p. > 360°. IR: 1703 (C=O), 1578, 1460, 1449, 1431, 1311, 1279, 1218, 1120, 1079, 1065, 1031, 923, 810, 755, 734, 729, 725, 678, 640 $cm^{-1}$. MS: 560 ($M^+$, 25), 438 (24), 424 (100), 423 (47), 396 (46), 394 (43), 392 (24), 364 (22) and Fig. 4. Daughters: 560 → 516, 483 (minor), 424 (predominant), 396, 392; 528 → 500; 516 → 483; 515 → 483; 499 → 467, 438; 470 → 438; 467 → 435; 438 → 406; 424 → 396, 391; 396 → 364, 351.

Compound **11a** (0.10 g, 0.18 mmol) was dissolved in dioxane (5 ml). $K_3[Fe(CN)_6]$ (0.15 g) and KOH (0.15 g) in water (10 ml) were added. The mixture was refluxed for 5 min, then cooled and the solid formed was collected. Yield 80 mg (80%) of **20** in all respects identical with the material above.

Compound **12a** (15 mg, 27 $\mu$mol) was dissolved in dioxane (1 ml). $K_3[Fe(CN)_6]$ (60 mg) and KOH (60 mg) in water (2 ml) were added and the mixture refluxed for 5 min. After cooling, the solid formed was collected, yield, 11 mg of yellow crystals. Both the starting material, as well as the product had impurities. However, by careful extraction with refluxing $CH_2Cl_2$, a residue (1.0 mg) remained, consisting of **23**. IR: 1690

(C=O), 1582, 1518, 1448, 1308, 1278, 752, 744, 726 cm$^{-1}$. MS: 560 (M$^+$, 10), 484 (17), 483 (18), 424 (100), 423 (61), 396 (42), 394 (35), 288 (18) and Fig. 5. Daughters: 560 → 532, 424 (predominant), 396 (very minor). Parents: 424 → 560; 484 → 512, 528.

### *Treatment of* 3(2H)-*benzo*[*b*]*thiophenone with* Br$_2$ *in* CS$_2$ (cf. *Ref.* 6)

3(2H)-Benzo[*b*]thiophenone (4.50 g, 30 mmol) was dissolved in CS$_2$ (15 ml). Br$_2$ (1.60 g, 10 mmol) in CS$_2$ (3 ml) was slowly added at room temp. The reaction was left under stirring for 30 min. Examination of the crude product by TLC with CH$_2$Cl$_2$–hexane (1 : 1) as eluent, showed a strong spot at $R_f = 0.24$ and a minor spot at $R_f = 0.61$ (yellow). The latter is also obtained from **10** in this system. A small amount of solid material was filtered off and discarded. The solvent was then allowed to evaporate. A yellow material was left, which after crystallizations from toluene–EtOH and CH$_2$Cl$_2$–hexane (1 : 1) yielded **22a** (1.60 g, 37%). At 165° crystals started to turn red, remaining yellow crystals melted at 181–183° (lit.[6] m.p. 198–199°). IR: 3215 (OH), 1665 (C=O), 1585, 1570, 1528, 1450, 1441, 1438, 1302, 1286, 1258, 1073, 810, 757, 740, 730, 668, 650 cm$^{-1}$. $^{13}$C-NMR (DMSO-$d_6$): 198.22 (s) and 63.82 (s). The aromatic C atoms resonated between 150.49 and 114.18. MS: 430 (M$^+$, 44), 296 (88), 281 (100).

Acetate **22b** was obtained by the general procedure. After purification by column chromatography with CH$_2$Cl$_2$–hexane (2 : 1), the yield was 78%, m.p. 171–173° (ether). IR: 1785 (C=O), 1695, 1598, 1585, 1575, 1450, 1430, 1355, 1287, 1186, 1175, 1166, 878, 869, 862, 856, 843, 833 cm$^{-1}$. MS: 472 (M$^+$, 3), 430 ([M−42]$^+$, 44), 296 (100), 293 (31), 281 (23), 253 (16), 221 (31) and Fig. 6. Daughters: 472 → 430, 412; 430 → 412, 401, 369, 296, 293, 281; 293 → 264. Parents: 221 → 253; 281 → 430; 293 → 430; 296 → 430; 369 → 401, 430; 401 → 430; 412 → 430, 472; 430 → 472.

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