Tetrahedron. Vol. 29, pp. 1379 to 1391. Pergamon Press 1973. Printed in Great Britain

HETEROCYCLIC TRIPTYCENES[1]

SYNTHESIS AND ULTRAVIOLET SPECTROSCOPY

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(*Received in the UK* 6 *December* 1972; *Accepted for publication* 16 *January* 1973)

Abstract—The synthesis of some heterocyclic triptycenes is reported. A study of the UV spectra of these and analogous compounds was undertaken. Two series of compounds were prepared: 9,10-bridged anthracene compounds and 5,12-bridged naphthacene compounds. The results from these studies alone are inconclusive. However if calculations are made, based on interannular π–π interactions between the aromatic rings in these systems, the calculated $N \rightarrow V_1$ transitions and longest wavelength absorption maxima give a straight line when plotted.

INTRODUCTION

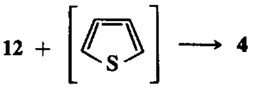
The UV spectrum of triptycene (**1**) has been interpreted in two different ways. On the basis of appreciable spectral difference between triptycene and triphenylmethane in absorption maxima as well as in extinction coefficient, Bartlett and Lewis[2] assume the presence of cross-ring interaction in triptycene. Wilcox, Jr., and Craig on the other hand calculated the UV spectrum of triptycene[3] and a few ring-substituted triptycenes[4] and concluded that the spectra of these compounds could be regarded to be superpositions of the three separate chromophores. To investigate the origin of these conflicting statements two series of triptycenes and related compounds were prepared of which only the character of one chromophore in one series was different.

In order to be certain, that the spectroscopic data would be limited to that due to the π-clouds of the aromatic rings, (not perturbed by an unknown influence of substituents) the synthesis of unsubstituted compounds was undertaken.

RESULTS

In order to be able to compare results of more than one series of compounds, we prepared the compounds that are depicted in Table 1. 9,10-Dihydroanthracene (**1**), 9,10-dihydro-9,10-ethanoanthracene (**2**), triptycene (**3**), 9,10-dihydro-9,10-ethenoanthracene (**5**), 5,12-dihydronaphthacene (**6**), 5,12-dihydro-5,12-(13-ethyl)ethanonaphthacene (**7**), benzotriptycene (**9**) and 4,11-dihydro-4,11-*o*-benzenoanthra[2,3-*b*]thiophene (**10**) were prepared according to literature methods (Table). The preparation of 4,9-dihydro-4,9-*o*-benzenonaphtho[2,3-*c*]thiophene (**4**) and 4,11-dihydro-4,11-*o*-benzenoanthra[2,3-*c*]thiophene (**8**) was less straightforward and follows herewith.

A Diels–Alder reaction between 3,4-dehydrothiophene (**11**) and anthracene (**12**) could give **4** in one step. However, although **11** has been mentioned in the literature,[13] its existence has not been proved.



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It is therefore necessary to form a thiophene ring from an initially formed Diels–Alder adduct of **12**. Many thiophenes have been made by a reaction of a diacid or its disodium salt with phosphorus sulfides.[14] A reaction between the disodium salt of **13**[15] and P_2S_5 did not give the expected product **4**. Instead anthracene (**12**), as a result of a retro Diels–Alder reaction, was formed in yields varying

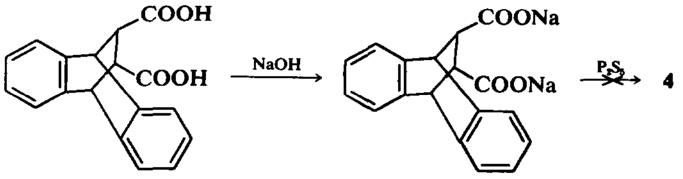

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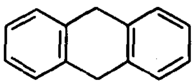
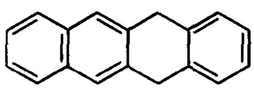
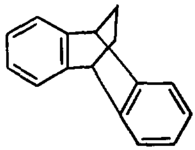
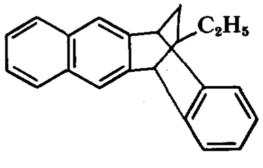
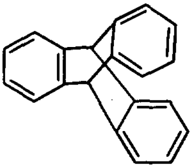
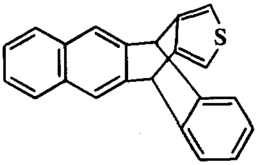
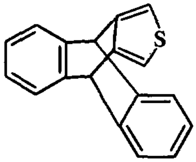
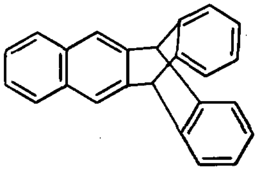
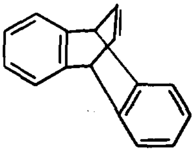
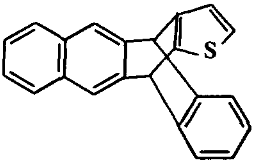
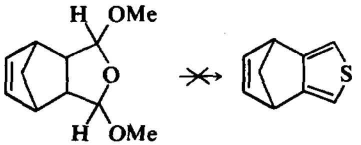
Table 1.

Compound	Structural Formula	m.p.	Lit. Value	Ref	Compound	Structural Formula	m.p.	Lit. Value	Ref
1		107·5–109	107·5	5	6		211–213	212	9
2		144–145	145–146	6	7		83–103	83–103	10
3		254–255	254–255·5	7	8		285–289		
4		268			9		263–266	256–257	11
5		117–118·5	118·5–119	8	10		267–270	267–270	12

from 43–80%, depending on reaction time and reaction temperature. Even if the disodium salt was heated at 240° for 1 hr without P_2S_5 anthracene (**12**) was formed in 89%, calculated on reacted starting material.

The synthesis of thiophenes from initially formed Diels–Alder adducts of 1,3-cyclohexadiene and cyclopentadiene has been studied extensively by Klunder.[16] He found, that, with one exception, methyl substituted thiophenes could be prepared from the Diels–Alder adducts of 1,3-cyclohexadiene and cyclopentadiene with hexene-2,5-dione. A reaction of these adducts or the hydrogenated ones with H_2S and HCl furnished the desired bicycloheterenes. Attempts to prepare the unsubstituted thiophenes in a similar way, starting from the Diels–Alder adducts of 1,3-cyclohexadiene and cyclopentadiene with fumaric dialdehyde failed; only polymeric products were obtained. Also a reaction of the Diels–Alder adduct of cyclopentadiene and acetal **14** with H_2S and HCl was unsuccessful.[17] The failure of this reaction has been attributed to the intermediacy of the dialdehyde **15**, which gives rise to polymerisation-reactions rather than a ring-closure reaction. It was thought that a Diels–Alder product with acetal **16** might give a carbomethoxy substituted thiophene because the intermediate product in the ring-closure reaction (a keto-aldehyde) might be more stable and less prone to polymerisation reactions.



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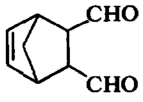

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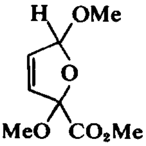

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Acetal **16** was prepared by electrolysis of methyl-2-furoate.[18] It was not possible to obtain a Diels–Alder adduct between anthracene (**12**) and **16**. We therefore decided to attempt the synthesis of a methylsubstituted thiophene from adduct **17**[19] and H_2S/HCl and to replace the Me groups by hydrogens using normal synthetic techniques. Compound **17** was prepared from anthracene (**12**) and *trans*-diacetylethylene (**18**)[20] in 78% yield. When anthracene was allowed to react with *cis*-**18** a mixture of 40% *cis*-adduct (**19**) and 60% *trans*-adduct (**17**) was obtained in 82% yield. The reaction was carried out with 1 mole of anthracene and 2 moles of *cis*-**18**. The excess of *cis*-**18** was recovered as a mixture of *cis*- and *trans*-**18**. This suggests that at the reaction temperature, *cis*-**18** isomerizes partly to *trans*-**18**. A ring-closure reaction of **17** and of a mixture of **19** and **17** with H_2S/HCl led to the desired Me substituted heterotriptycene **20** in 83% and 75% yields respectively.* The degradation of this heterotriptycene to the unsubstituted one (**4**) was performed nearly analoguously to a reaction sequence given by Griffing and Salisbury.[22] These reactions are depicted below.

The dibromide **21** was obtained in 84% yield by a reaction of **20** with NBS and dibenzoylperoxide in carbontetrachloride according to the method of Zwanenburg.[23] The dibromide was converted to the diacetate **22** in 87% yield. Hydrolysis of diacetate **22** with sodium ethoxide to the non-isolated diol (an IR spectrum of this intermediate showed a broad absorption at 3450 cm^{-1}, whereas the CO absorption at 1730 cm^{-1} of the diacetate had disappeared), followed by oxidation with $KMnO_4$ furnished the diacid in 38% overall yield. Decarboxylation of this diacid (**23**) with CuO in quinoline[24] afforded the unsubstituted heterotriptycene **4** in 56% yield. The structure of the products **21**, **22**, **23** and **4** was supported by the spectral data and correct elemental analysis (**23** was analysed as the dimethylester) and by the reaction sequence followed.

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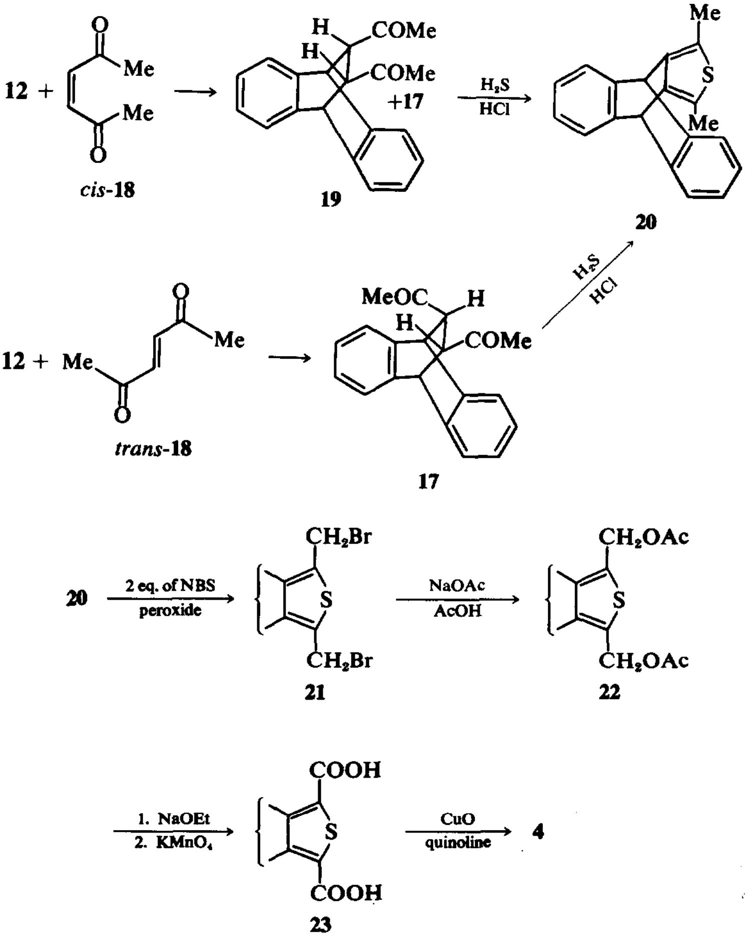
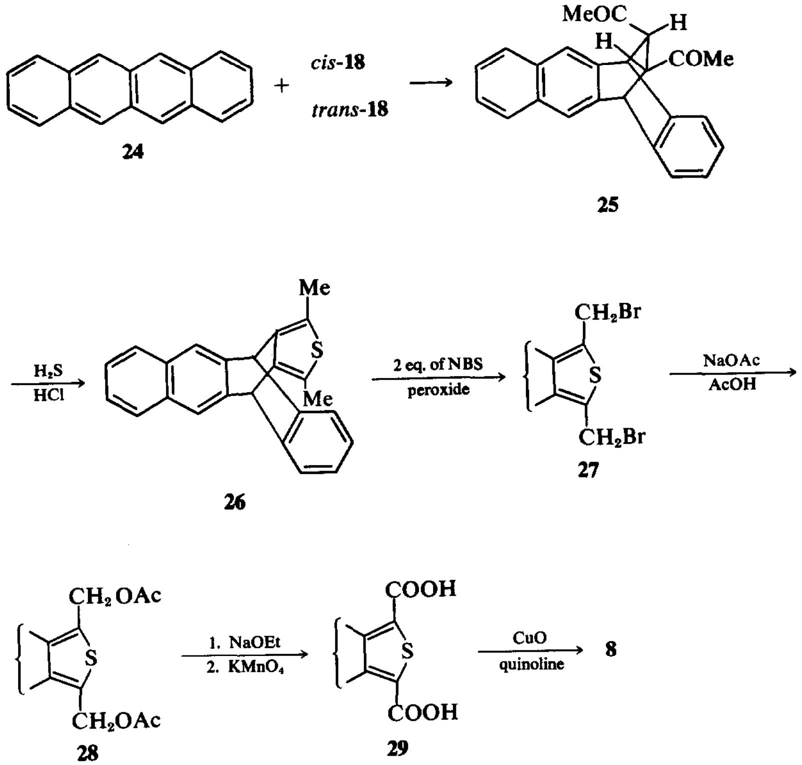
*When this work had been completed, the synthesis of **20** was reported.[21] Different reaction conditions and reagents were used and the yield of **20** was only 8%, based on anthracene.



The synthesis of the heterotriptycene **8** was performed exactly analogous to that of **4**. The adduct between **24** and *trans*-**18** (**25**) was obtained in 70% yield when the two components were heated for 10 min at 200° in a nitrogen atmosphere. A reaction between **24** and *cis*-**18** also afforded the pure *trans*-adduct **25**, as could be concluded from the NMR spectrum and the m.p. The *trans*-adduct was converted into the heterotriptycene **26** in 80% yield by a ring-closure reaction with H_2S and HCl. The same sequence as given for the synthesis of **4** was then applied. Bromination of **26** gave the dibromide **27** in 78% yield. This dibromide was converted into the diacetate **28** in 92% yield. Hydrolysis of **28** with sodium ethoxide followed by oxidation with $KMnO_4$ gave the diacid **29** (in 18% yield), which was decarboxylated to furnish the heterotriptycene **8** (in 43% yield). The structure of compounds **25**, **26** and **8** was supported by the spectra and the elemental analysis. No elemental analysis were obtained for compounds **27**, **28** and **29** owing to a lack of material. If we compare the NMR and MS spectra of **27**, **28** and **29** with those of **21**, **22** and **23**, we must conclude that the assigned structures are correct. In the NMR spectra (Table 2) the same absorptions are observed for the protons of the thiophene-substituents when comparing **21**, **27** and **22**, **28**. The bridgehead protons in **29** are shifted 0·13 ppm to lower field when compared with those in **23**. The differences between these protons in **28** and **22** is 0·12 ppm and that between the bridgehead protons in **27** and **21** is 0·11 ppm. The mass spectra (Table 3) clearly show (apart from a correct parent peak) similar fragmentation patterns.



DISCUSSION

Wilcox has studied the UV spectrum of triptycene in detail.[3] He found that the 0·1-eV bathochromic shift and the enhanced absorptivity of the α-band* when comparing triptycene to o-xylene, could be explained by making assumptions, which do not require interbenzene resonance interactions. This model has also been used successfully for the interpretation of the UV spectra of bridgehead derivatives of 2,5-dihydroxytriptycenes.[4]

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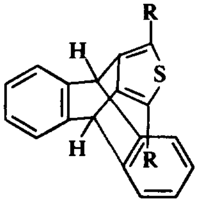
*The notation for UV spectra, used in this chapter is that of Clar.[25] The long wavelength parts of the spectra of condensed aromatic hydrocarbons show the following bands in order of decreasing wavelength:

1. α-band: Weak (log ε 2 to 3) consisting of sharp peaks.
2. p-band: Medium strong (log ε 4 to 5) usually at least three vibrational peaks.
3. β,β′ etc bands: Strong (log ε 4 to 6) with little fine structure.

Table 2.



Compound		NMR-absorptions in ppm (τ)		
		$—CH_2—R'$	$—CH_2OCOCH_3$	Bridgehead protons
$R = CH_2Br$	21	5·38	—	4·64
	27	5·37	—	4·53
$R = CH_2OCOCH_3$	22	4·78	8·00	4·54
	28	4·75	8·00	4·42
$R = COOH$	23	—	—	3·80
	29	—	—	3·67

However, these results do not imply that all spectra of benzobicyclooctane systems are alike. In Tables 4 (derivatives of 9,10-dihydroanthracene) and 5 (derivatives of 5,12-dihydronaphthacene) the UV spectra of compounds **1–10** and **30*** are collected.

From the data, given in these Tables it can be concluded:

1. If 9,10-dihydroanthracene (**1**) and 5,12-dihydronaphthacene (**6**) are chosen as basis compounds the magnitude of the bathochromic shift of λ_{max} of the α-band depends upon the bridge that is attached across the meso-C atoms. This shift is more or less related to the bond-order of the attached moiety: if $p = 0{\cdot}00$ (**2** and **7**) no shift is observed whereas if p increases to 1·00 (**5** and **30**) a shift of 9 and 4·5 nm respectively of the longest wavelength absorptions is observed. The p-bands of the compounds listed in Table 5 do not show an appreciable shift.

2. The extinction-coefficient ϵ of the α-bands is not increased if aliphatic moieties are attached to the meso-C atoms in **1** and **6**; when moieties containing pi-orbitals are attached there is a 3–4 fold increase. Again, no such effect is observed in the p-bands of the compounds tabulated in Table 5.

These bathochromic shifts and enhanced absorptivities of the α-bands might be due to:

1. Differences in ring strain of the described compounds (which all are derivatives of bicyclo-[2.2.2]octane).

2. Interactions of locally excited states[27] (without intervoking interaromatic interactions).

3. A "through-space"-resonance interaction.

Ad 1. The influence of ring strain on the UV spectra of aromatic compounds has been studied in detail.[28] Generally it is conceded that a change of ring strain in an aromatic molecule does not influence the positions of the absorption-maxima.

Typical examples are given in Tables 6, 7 and 8.

From the results depicted in these Tables it can be concluded:

1. No regular batho- or hypsochromic shift is observed if the strain in the molecules increases.

2. The absorptivity is enhanced 5- to 10-fold in cases where substituted benzenes are involved (Tables 6 and 8), but negligibly in the case where substituted naphthalenes are involved (Table 7).

This means that the (very small) differences in ring strain do not explain the bathochromic shifts, observed in the α-bands of the UV spectra of the compounds depicted in Tables 4 and 5.

Ad 2. If the interaction of locally excited states could explain the UV spectra of triptycene sys-

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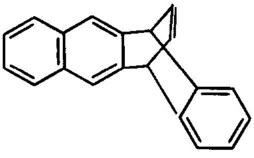
*A synthesis of 9,10-dihydro-9,10-ethenonaphthacene (**30**) was not successfull.



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We therefore report the values given by Klanderman for the UV spectrum of **30**.[26]

Table 3. Mass spectra

21		27		Fragments	22		28		Fragments	23		29		Fragments
Peak	rel. ab. (%)	Peak	rel. ab. (%)		Peak	rel. ab. (%)	Peak	rel. ab. (%)		Peak	rel. ab. (%)	Peak	rel. ab. (%)	
448	3	498	10	parent (Br 81,81)	404	75	454	100	parent	349	28	399	5	P + 1
446	6	496	16	P_2(Br 81,79)	345	28	395	28	P—CO_2CH_3(M)	348	100	398	15	parent
444	3	494	9	P_3(Br 79,79)	303	28	353	12	N + 1	318	26	368	5	P—CH_2O
367	100	417	100	P_1—Br 81	302	100	352	37	M—$COCH_3$(N)	303	23	353	6	P—COOH(M)
365	100	415	100	P_3—Br 79	285	44	335	18	M—CO_2CH_3—H	302	32	352	8	P—CO_2H_2
286	100	336	32	P—Br_2(M)	284	36	334	17	M—CO_2CH_3—H_2	259	31	309	12	M—CO_2
285	62	335	25	M—H	271	44	321	21	M—$CH_2CO_2CH_3$—H	258	40	308	14	P—2 × CO_2H
272	38	322	16	M—CH_2(N)	239	29	289	11	M—$C_3H_5O_2$—S	178	77	228	20	P—$C_6H_2SO_4$
252	34	302	16	M—H_2S	178	23	228	17	P—$C_{10}H_{10}SO_4$					
228	71	278	13	N—CS										

Table 4. UV spectra in cyclohexane

Compound	λ_{max} (nm) (log ϵ)				Bond order of
1	254·5	258·5	264·5	271	—
	(2·83)	(2·87)	(3·03)	(3·03)	
2		258	265·5	272·5	single bond
		(2·91)	(3·17)	(3·28)	0·00
3		264·5sh	271	278·5	benzene
		(3·26)	(3·53)	(3·61)	0·67
4		265	268	277·5	3,4-thiophene
		(3·71)	(3·76)	(3·57)	0·56
5	252·5	265·5	272·5	280	double bond
	(3·00)	(3·00)	(3·33)	(3·49)	1·00

tems the compounds should show chromophoric additivity.[3,4] At first glance, this is not true for compounds **8** and **10**. The α-band of heterotriptycene **8** is displaced 2·5 nm towards longer wavelength compared to **10**, whereas 2,3-dimethylthiophene (one of the chromophores in **8**) absorbs at 4 nm lower wavelength than 3,4-dimethylthiophene (one of the chromophores in in **10**) does.* Due to the small differences observed in the UV spectra of the compounds depicted in Tables 4 and 5 it is not possible to decide on the basis of UV spectroscopy alone whether "through-space"-resonance effects are operating in triptycene systems. However, the CD spectrum of an optically active triptycene[10] had furnished us with support for the contention that weak interaction between the three rings existed. Therefore, it was of interest to see whether simple Hückel-MO calculations, based on a model that includes interannular overlap of π-orbitals in different aromatic rings would predict the observed changes in the UV spectra.

The UV spectra of triptycene (**3**) has been calculated by use of the Longuet-Higgins and Murrell model.[27] This model predicts no shift for the α-band of triptycene.[3] The observed shift of 6·5 nm comparing the α-bands of triptycene and *o*-xylene was explained by making assumptions that do not include interbenzene resonance interactions. Using the same model, barrelene (**32**) was cal-

Table 5. UV spectra in cyclohexane

Compound	λ_{max} (nm)	(log ϵ)							Bond order of
	β-band		*p*-band				α-band		
6	224	(4·95)	251sh	(3·50)	280	(3·77)	305·5	(2·82)	
	230	(5·09)	262sh	(3·70)	290	(3·58)	315·5	(2·50)	—
			271	(2·82)			319·5	(2·77)	
7	217sh	(4·60)	259	(3·85)	277·5	(3·90)	305·5	(2·87)	single bond
	232·5	(4·93)	267	(3·95)	286·5	(3·68)	317sh	(2·57)	0·00
	236sh	(4·89)	271	(3·93)	288·5	(3·65)	319·5	(2·90)	
8							295sh	(2·97)	
	229	(4·81)	256	(4·51)	288	(3·66)	302	(2·81)	3,4-thiophene
							308·5	(3·15)	
	234·5	(4·82)	266sh	(4·19)			315	(2·83)	0·56
	256	(4·51)	276	(4·05)			322·5	(3·28)	
9	226·5	(4·84)	259·5	(4·04)	288	(3·69)	295	(2·94)	benzene
							301·5	(2·82)	
	234	(4·78)	267·5	(4·28)			308·5	(3·12)	0·67
							314·5	(2·81)	
	242·5	(4·44)	276·5	(4·12)			322·5	(3·24)	
10	225sh	(4·79)	254	(4·29)	277·5	(4·26)	297·5	(2·99)	2,3-thiophene
							304	(2·92)	
	231·5	(4·89)	258	(4·28)	286	(3·75)	310·5	(3·26)	0·78
							317	(2·95)	
			268·5	(4·29)			325	(3·39)	
30	225	(4·67)	257	(3·97)	288	(3·68)	297	(2·86)	double bond
	234	(4·78)	268	(4·09)			310	(3·11)	1·00
	242	(4·86)	276	(4·13)			324	(3·23)	

(sh = shoulder).

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*Ref. 14, p. 101:
2,3-dimethylthiophene has λ_{max} = 234 nm (log ϵ = 3·78),
3,4-dimethylthiophene has λ_{max} = 238 nm (log ϵ = 3·76).

Table 6. UV spectra in cyclohexane

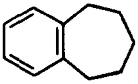
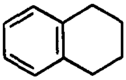
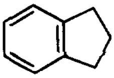
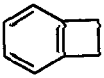
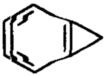
Compound	λ_{max} (nm)	(log ϵ)				Ref.
		257 (2·28)	263·5 (2·48)	268 (2·35)	271 (2·34)	29
		258 (2·53)	263 (2·62)	266·5 (2·75)	274 (2·76)	29
		253 (2·56)	261·5 (2·94)	267·5 (3·09)	274 (3·19)	29
		255 (2·86)	260 (3·09)	265·5 (3·28)	271·5 (3·27)	30
	250 (2·65)	260 (3·03)	264·5 (3·23)	269·5 (3·32)	275·5 (3·42)	31

Table 7. UV spectra

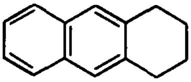
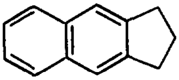
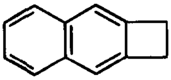
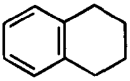
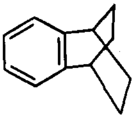
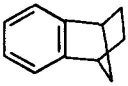
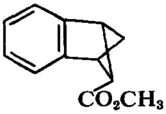
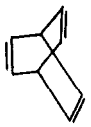
Compound	solvent	λ_{max} (nm)		(log ϵ)	Ref.
	cyclohexane	271 (3·83) 280·5 (3·89) 289 (3·78)	301 (3·38) 307 (3·20) 313·5 (2·94)	316·5 (2·85) 320·5 (3·29)	32
	cyclohexane	270 (3·69) 279·5 (3·72) 290 (3·55)	306·5 (3·10) 313 (2·90) 320·5 (3·19)		32
	ethanol	267 (3·68) 278 (3·78) 290 (3·63)	304 (3·06) 311 (2·85) 318 (3·21)	shoulders at 250, 259, 286	33

Table 8. UV spectra

Compound	Solvent	λ_{max} (nm)		(log ϵ)		Ref.
	cyclohexane	258 (2·53)	263 (2·62)	266·5 (2·75)	274 (2·34)	29
	n-heptane		254·7 (2·56)	261·2 (2·73)	268·0 (2·87)	34
	n-heptane	252·3 (2·56)	258·7 (2·80)	265·0 (2·98)	271·8 (3·03)	34
	n-heptane		260·5 (2·80)	267 (2·93)	274 (2·97)	35

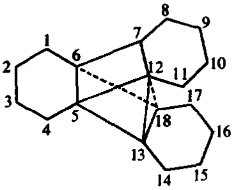
culated to have absorption maxima at 215 and 184 nm.[36]



32

Zimmerman and Paufler[37] who achieved the first synthesis of this compound, report values of 239 and 208 nm. By taking non-zero resonance integrals between the nonconjugated carbonatoms of barrelene the calculated values of the absorption maxima are very close to the experimental ones (Zimmerman:[38] 241 and 207 nm, Paldus:[39] 239 and 207 nm).

We have therefore calculated the MO's of triptycene (**3**) using variable values for the resonance integrals of nonconjugated atoms.*



If these values are varied from 0·05β_{CC} (i.e. $\beta_{6,7} = \beta_{5,12} = \beta_{6,18} = \beta_{5,13} = 0{\cdot}05\beta_{CC}$ and $\beta_{7,18} = \beta_{12,13} = -0{\cdot}05\beta_{CC}$ because of a Möbius-type of system[40]) to 0·5β_{CC}, we find for the N → V_1 transitions: $\Delta E(\beta) =$ 1·924 (0·05β_{CC}), 1·845 (0·10β_{CC}), 1·595 (0·25β_{CC}) and 1·172 (0·50β_{CC}), whereas benzene is calculated to have $\Delta E(\beta) = 2{\cdot}000$. If the energy-levels of benzotriptycene (**9**) are calculated with resonance integrals of 0·5β_{CC} we find $\Delta E(\beta) = 1{\cdot}101$ for the N → V_1 transition, whereas naphthalene is calculated to have $\Delta E(\beta) = 1{\cdot}236$. This means that the effect of including resonance integrals is larger in triptycene than in benzotriptycene, in agreement with the observed shifts of the longest wavelength component of the α-bands of 6·5 and 2·5 nm respectively, compared to *o*-xylene and 2,3-dimethylnaphthalene.[3]

The N → V_1 transitions of compounds **4**, **5**, **8**, **30** and **10** were also calculated with the same value of the resonance integral as for **1** and **17** (0·5β_{CC}).† The results are listed in Table 9 together with the experimentally found longest wavelength component of the α-bands.

If the experimental values are plotted against the calculated ones we find two regression lines (one for the bridged anthracene compounds and one for the bridged naphthacene compounds‡) that show a good correlation (Fig 1).

The slopes of the lines were calculated by the least square method and we find benzene-like (a) E_{exp} (eV) = 0·137 $\Delta E(\beta)$ + 4·301 (correlation coefficient 0·994). naphthalene-like (b) E_{exp} (eV) = 0·189 $\Delta E(\beta)$ + 3·640 (correlation coefficient 0·992).

The slopes of these lines do not correspond to an acceptable value for β (1–3 eV) because the chosen resonance integral (0·5β_{CC}) is certainly incorrect. If the value of this integral is changed, we note the following

a. Above 0·3β_{CC} the good correlation between all compounds holds, although the slope is not corresponding to an acceptable value for β.

b. Below 0·3β_{CC} the slopes increase with decreasing resonance integral, but the good correlation vanishes, which is probably due to the very small differences in the calculated figures.

From these calculations it might be proposed

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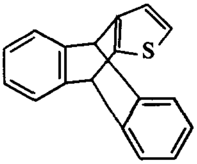
*The calculations were performed with a HMO-computer program, written by Dr. J. W. van Reyendam and Dr. P. B. Koster. The following parameters were used: $\alpha_S = \alpha_C + \beta_{CC}, \beta_{CS} = 0{\cdot}7\beta_{CC}$.

†By inspection of the secular determinant it can easily be concluded that the place of the nodes even in the case of (hetero) triptycenes that do not have D_{3h} symmetry is irrelevant for the values of the energy levels.

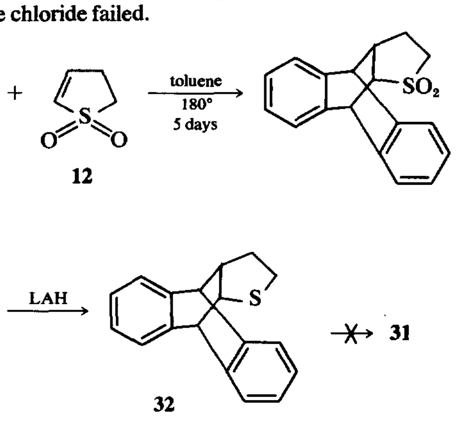
‡Several attempts were made towards the missing compound in the anthracene series, i.e. 4,9-dihydro-4,9-*o*-benzenonaphtho[2,3-b]thiophene (**31**).



31

Since naphtho[2,3-b]thiophene does not react with benzyne,[41] other methods had to be employed.

Reactions analogous to the method of Hauptman[42] all failed. A route analogous to that of Ditmar[43] was successful. However, all attempts to dehydrogenate compound **32** either directly or via the chlorosulfoxide or the chloride failed.



From the regression line compound **31** is calculated to have a longest wavelength absorption maximum at 279·5 mm.

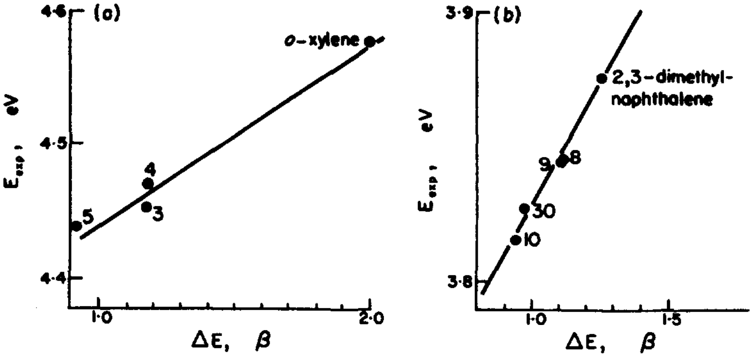


Fig 1.

Table 9.

Compound	E (eV) α-band	ΔE (β) N → V_1	Compound	E (eV) α-band	ΔE (β) N → V_1
o-xylene	4·576	2·000	2,3-dim. naphthalene	3·875	1·236
4	4·469	1·174	8	3·845	1·102
3	4·452	1·172	9	3·845	1·101
5	4·429	0·915	30	3·827	0·972
			10	3·815	0·937

that a small overlap is responsible for the differences observed in the UV spectra.

EXPERIMENTAL

M.ps were determined on a Reichert hot-stage apparatus and are uncorrected. B.ps are uncorrected. IR spectra were taken on a Unicum SP 200, only significant and/or large peaks are reported. Mass spectra were obtained with an AEI MS 902 instrument by Mr. A. Kiewiet; only peaks with significant relative abundancies are given. NMR spectra were determined with a Varian A-60 or A-60 D, using TMS as an internal standard. The chemical shifts are reported in ppm on the τ-scale. UV spectra were taken on a Zeiss PMQ II unless otherwise stated; only analytically pure samples were measured. If not mentioned cyclohexane Uvasol (Merck) was used as a solvent. GLC was performed on an F and M 810. Elemental analyses were carried out in the microanalytical department of this laboratory under supervision of Mr. W. M. Hazenberg by Mr. H. Draayer, Mr. J. Ebels and Mr. J. Vos. Column chromatography was performed on alumina (neutral, activity 1, Merck A. G.) or silica gel (B.D.H.) with dried and distilled eluents.

Attempted reaction between the sodium salt of **13** *and phosphoruspentasulfide*

A mixture of 4·2 g (12·5 mmole) of the disodium salt of **13**, 5 g dry sand and 4·0 g P_2S_5 was heated at 240° for 1–6 hr. After cooling, 60 ml 20% NaOHaq was added cauteously and the resulting black emulsion was filtered and the filtrate extracted with benzene. The benzene layer was dried over $CaCl_2$ and concentrated, leaving 2·5–1 g of a yellow solid, that was crystallized from EtOH to give **12** as colourless leaflets, m.p. 211–213° (lit. Handbook 216·2–216·4°).

Methyl-2,5-dimethoxy-2,5-dihydro-2-furoate (**16**)

A soln of 18·25 g (0·145 mole) methyl-2-furoate, b.p. 70–71°/11 mm (lit.[44] b.p. 181°) in 145 ml MeOH and 1·0 ml conc H_2SO_4 was electrolysed in a cell, containing a platina-anode and -kathode, for 24 hr at −15°. The voltage over the cell was kept at 17V during the first 4 hr (I = 2·2A → 1·7A) and then raised to 19V (I = 1·8A → 1·0A). The colourless soln was then added quickly to the reaction product of 0·95 g Na and 15 ml MeOH. The MeOH was removed *in vacuo* and the residue distilled twice to furnish 13·53 g (0·072 mole, 50%) of **16** as a colourless liquid, b.p. 115–118°/8 mm, $n_D^{20} = 1{\cdot}4497$ (lit.[18] 68%, b.p. 119–121°/13–14 nm, $n_D^{25} = 1{\cdot}4476$). Gaschromatographical analysis (carbowax) showed the compound to be 95% pure.

Attempted reaction between acetal **16** *and anthracene* (**12**)

a. A mixture of 2·0 g (10·8 mmole) of **12**, 2·8 g (15·2 mmole) of **16**, $n_D^{20} = 1{\cdot}4497$, 0·2 ml conc HCl and 10 ml water was stirred at room temp for 2 hr and at 40° for 18 hr. The ppt was filtered off and dried to give 1·7 g = 85% unreacted **12** and the filtrate was concentrated, leaving 0·2 g unidentified brown oil.

b. A mixture of 10·5 g (0·056 mole) of **16**, $n_D^{20} = 1{\cdot}4497$, 10·3 g (0·056 mole) of **12** and a few crystals of hydroquinone was heated in a sealed tube at 160° for 25 hr, 180° for 18 hr and 220° for 6 hr. The contents of the tube were dissolved in chloroform and chromatographed over alumina with benzene. The eluate was concentrated, leaving 9·7 g (92%) of **12** as a white solid, m.p. 217–218° (lit. Handbook 216·2–4°).

cis- *and* trans-*Diacetylethylene* (**18**)

A soln of 30 g (0·312 mole) 2,5-dimethylfuran (b.p. 92–94°) and 62 g anhyd AcOK in 400 ml MeOH was cooled to 0°. A soln of 15·5 ml Br_2 in 195 ml MeOH was added at such a rate, that the temp did not exceed 0° (1 hr). After standing for 2 hr at 0°, the turbid mixture was poured into 800 ml sat NaCl aq and the resulting soln was filtered and extracted with chloroform. The organic layer was dried over $CaCl_2$ and concentrated. The residue was distilled to give 20·5 g (0·13 mole, 42%) acetal, b.p. 49–51°/10 mm, n_D^{19} = 1·4345 (lit.[20] b.p. 59°/16 mm, n_D^{16} = 1·4312) and 6·4 g (0·06 mole, 18%) of *cis*-**18**, b.p. 83–85°/10 mm (lit.[20] b.p. 92°/16 mm). The residue from the distillation was sublimed to give 1·2 g (0·01 mole, 4%) of *trans*-**18**, m.p. 77–78° (lit.[20] m.p. 76–77°). The acetal was converted to *cis*-**18** (10·6 g, 73%), according to the method of Lévisalles.[20]

9,10-*Dihydro*-9,10(11,12-*transdiacetyl*)*ethanoanthracene* (**17**)

A mixture of 5·0 g (0·028 mole) of **12** and 6·3 g (0·056 mole) of *trans*-**18**, m.p. 77–78° was heated in a N_2 atm for 1 hr at 200°. The dark residue was cooled, shaken with ether and filtered. The white residue (8·0 g) was crystallized from EtOH to give 6·3 g (0·022 mole, 78%) white needles, m.p. 217–218·5° (lit.[19], 80%, m.p. 211–213°); IR (KBr): 1690, 1340, 1250, 1160, 760, 740 cm^{-1}; NMR ($CDCl_3$): τ = 2·60–3·03 (m, 8H), 5·33 (m, 2H), 6·53 (m, 2H), 7·78 (s, 6H).

9,10-*Dihydro*-9,10-(11,12-*cis- and transdiacetyl*)*ethanoanthracene* (**19** *and* **17**).

From a mixture of 6·6 g (0·037 mole) of **12** and 8·2 g (0·073 mole) *cis*-diacetylethylene (b.p. 85–87°/11 mm) was obtained 8·7 g (82%, 0·030 mole) of a white solid, m.p. 185–214°; NMR ($CDCl_3$): τ = 2·60–3·00 (m, 13H), 5·33–5·40 (m, 4H), 6·52 (m, 2H), 6·78 (m, 1H), 7·78 (s, 6H), 7·97 (s, 4H).

4,9-*Dihydro*-1,3-*dimethyl*-4,9-o-*benzenonaphtho*[2,3-c]-*thiophene* (**20**)

a. *From* **17**. A soln of 1·45 g (5 mmole) of **17**, m.p. 217–218·5° in 100 ml MeOH and 50 ml $CHCl_3$ was heated to 55°. While stirring, a mixture of H_2S and HCl was bubbled through the soln for 3 hr. The violet coloured mixture was poured into water, the chloroform layer was separated and washed with a 2N NaOH and water and dried. The chloroformlayer was filtered and concentrated, leaving 1·4 g yellow product. This product was crystallized from EtOH/$CHCl_3$, yielding 1·19 g (4·3 mmole, 83%) white crystals, m.p. 278–280°. (Found: C, 83·2; H, 5·7; S, 11·2. Calcd. for $C_{20}H_{16}S$: C, 83·33; H, 5·56; S, 11·11%); IR (KBr): 1180, 1010, 750, 730 cm^{-1}; NMR ($CDCl_3$): τ = 2·65–3·13 (m, 8H), 4·90 (s, 2H), 7·68 (s, 6H); UV: λ_{max} = 238 nm (log ϵ 4·07), 263·5 (3·72), 268·5 (3·70), 278 (3·55); Ms: m/e = 288, 287, 272, 258, 239, 229, 211, 178, 135·5, 136, 128, 120, 119, 113, 88, 69, 44.

b. *From a mixture of* **17** *and* **19**. From 7·8 g (26·7 mmole) of a mixture of **17** and **19**, m.p. 185–214° was obtained in the same way as described under (a) 5·8 g (20 mmole, 75%) of **20**, m.p. 276–278°.

4,9-*Dihydro*-1,3-*dibromomethyl*-4,9-o-*benzenonaphtho*-[2,3-c]*thiophene* (**21**)

To a soln of 8·7 g (0·030 mole) of **20**, m.p. 276–278° in 230 ml boiling tetra were added 11·2 g (0·063 mole) N-bromosuccinimide, m.p. 166–172° and 0·1 g dibenzoylperoxide. The mixture was refluxed for 20 min and filtered hot. The residue was dried, yielding 5·7 g (92%) succinimide, m.p. 123–125°. The filtrate was cooled and the resulting ppt filtered off and dried to give 11·3 g (25·4 mmole, 84%) white solid, m.p. 220° (d). IR (KBr): 1700, 1460, 1190, 750 cm^{-1}; NMR ($CDCl_3$): τ = 2·53–3·03 (m, 8H), 4·64 (s, 2H), 5·38 (s, 4H); Ms: m/e = 448 (rel. ab. 3·0%), 446 (5·5), 444 (2·9), 368 (23·6), 367 (100·0), 366 (23·6), 365 (100·0), 321 (27·5), 287 (31·5), 286 (100·0), 185 (61·8), 271 (38·2), 252 (33·9), 228 (71·3), 178 (13·9).

An analytically pure sample was prepared by dissolving a small amount in benzene, extracting the benzene layer with 1N HCl and crystallizing the residue obtained from concentration of the dried benzene layer, a few times from CCl_4. (Found: C, 54·0; H, 3·3; S, 7·2. Calcd. for $C_{20}H_{14}Br_2S$: C, 53·84; H, 3·16; S, 7·19%); UV: λ_{max} = 278 nm (log ϵ = 4·24).

4,9-*Dihydro*-1,3-*diacetoxymethyl*-4,9-o-*benzenonaphtho*-[2,3-c]*thiophene* (**22**)

A mixture of 1·7 g (3·8 mmole) of **21**, 0·95 g anhyd NaOAc and 10 ml AcOH was heated for 2 hr at 80°. The brown mixture was poured onto a water-ice mixture and the resulting ppt was taken up in ether. The ether layer was washed with three 100 ml portions of sat $NaHCO_3$aq and two 50 ml portions water. The ether layer was dried and concentrated leaving 1·34 g (3·3 mmole, 87%) yellow solid, m.p. 136–143°; IR (KBr): 1730, 1230, 1020, 750 cm^{-1}; NMR ($CDCl_3$): τ = 2·55–3·07 (m, 8H), 4·45 (s, 2H), 4·78 (s, 4H), 8·00 (s, 6H); MS: m/e = 404 (rel. ab. 75·0%), 345 (28·4), 303 (28·0), 302 (100·0), 285 (43·6), 284 (36·4), 272 (20·8), 271 (44·1), 239 (29·2), 226 (22·5), 178 (29·2).

An analytically pure sample was obtained by crystallizing 500 mg of the crude product many times from hexane. This furnished colourless plates, m.p. 160–163°. (Found: C, 71·0; H, 5·0; S, 8·0. Calcd. for $C_{24}H_{20}SO_4$: C, 71·27; H, 4·98; S, 7·93%); UV (Cary 15): λ_{max} = 316·5 nm (log ϵ = 1·97), 305·5 (2·14), 279 (4·04), 272·5 (4·00), 253 (4·30), 237 (4·35), 221 (4·89).

4,9-*Dihydro*-4,9-o-*benzenonaphtho*[2,3-c]*thiophene*-1,3-*dicarboxylic acid* (**23**)

To the reaction product of 64 mg Na and 20 ml abs EtOH was added 4·3 g (10·7 mmole) finely ground **22**. The mixture was shaken until soln was complete (15 min) and then set aside for 140 hr. After evaporation of the solvent, the residue was dissolved in 30 ml abs EtOH, filtered and the filtrate concentrated. The residue (3·3 g) was stirred for 4 hr at 35° with a soln of 2·4 g KOH in 30 ml water and the mixture left overnight. To the cooled (0°) mixture was added the next day 4·9 g powdered $KMnO_4$ in small portions over a period of 4·5 hr. Excess permanganate was destroyed with EtOH and the brown mixture was filtered. The filtrate was acidified with 6N HCl and the ppt taken up in ether. Evaporation of the ether left 1·3 g (4·0 mmole, 38%) yellow solid; IR (KBr): 3100, 1690, 1420, 1280, 1160 cm^{-1}; NMR (CD_3OD): τ = 2·52–2·73 (q, 4H), 2·92–3·07 (q, 4H), 3·80 (s, 2H); MS: $m/e = 349$ (rel. ab. 28·3%), 348 (100·0), 318 (25·5), 303 (22·6), 302 (31·6), 259 (30·7), 258 (39·2), 178 (76·9), 129 (22·6), 58 (82·6), 57 (66·0), 55 (28·3).

The diacid was analysed as the diester that was prepared by a reaction of **23** with 2 equiv diazomethane. The crude material was purified by chromatography over alumina with benzene and crystallization of the concentrated eluate from MeOH. The white needles had m.p. 227–229°. Found: C, 70·6; H, 4·3; S, 8·3. Calcd. for $C_{22}H_{16}O_4S$: C, 70·20; H, 4·29; S, 8·52%); IR (nujol): 1720, 1270 cm^{-1}; NMR ($CDCl_3$): $\tau = 2{\cdot}50$–3·05 (m, 8H), 3·82 (s, 2H), 6·12 (s, 6H); MS: $m/e = 378$ (rel. ab. 27·5%), 377 (63·7), 376 (100·0), 347 (22·6), 346 (41·1), 345 (48·0), 344 (29·4), 330 (28·4), 318 (23·5), 317 (27·5), 285 (29·4), 284 (31·3), 273 (26·5), 259 (23·5), 258 (72·6), 257 (40·2), 256 (22·6), 245 (20·6), 213 (47·1), 178 (37·3), 83 (22·6), 59 (48·0); UV (Cary 15, chloroform): $\lambda_{max} = 327$ nm (log $\epsilon = 3{\cdot}94$), 313 (4·00), 300sh (3·79), 286 (4·16), 277 (4·25).

4,9-*Dihydro*-4,9-o-*benzenonaphtho*[2,3-c]*thiophene* (**4**)

A finely ground mixture of 600 mg (1·71 mmole) of **23** and 1200 mg CuO was mixed with 15 ml quinoline. This mixture was heated at 230° (external temp) until the evolution of gas stopped (4 min), cooled and filtered. The filtrate was diluted with chloroform and extracted with 1N HCl until basification of the acidic layer gave no visible turbidity. The residual chloroform layer was washed with a sat $NaHCO_3$aq and with water and dried over $CaCl_2$. The dark red filtrate was chromatographed over alumina with benzene, yielding 250 mg (0·96 mmole, 56%) white solid. This solid was crystallized twice from EtOH to furnish 210 mg white plates, m.p. 268°. (Found: C, 82·9; H, 4·6. Calcd. for $C_{18}H_{12}S$: C, 83·05; H, 4·64%); IR (KBR): 1480, 1450, 830, 800, 750, 740; NMR ($CDCl_3$): $\tau = 2{\cdot}59$–3·07 (m, 8H), 3·14 (s, 2H), 4·69 (s, 2H); UV: see Table 4; MS: $m/e = 261$ (rel ab. 22·3%), 260 (100·0), 259 (83·5), 258 (35·1), 215 (22·9), 129 (29·3).

5,12-*Dihydro*-5,12-(13,14-trans *diacetyl*)*ethanoanthracene* (**25**).

a. *From* cis-**76**. A mixture of 4·0 g (17·5 mmole) of **24**, 3·9 g (35·0 mmole) *cis*- **18**, $n_D^{24} = 1{\cdot}4320$ was heated in a N_2 atm for 10 min at 200°. The cooled residue was shaken with ether, filtered and the filtrate concentrated to give 2·5 g solid residue. This residue was crystallized from cyclohexane to afford 1·2 g *trans*-**18**, m.p. 70–75°. The non-ether soluble material was crystallized from EtOH to give 4·04 g (11·8 mmole, 70%) white needles, m.p. 196–198°. (Found: C, 84·7; H, 6·0. Calcd. for $C_{24}H_{20}O_2$: C, 84·68; H, 5·92%); IR (KBr): 1680, 1340, 1160, 750 cm^{-1}; NMR ($CDCl_3$): $\tau = 2{\cdot}25$–2·98 (m, 10H), 5·21 (br.s, 2H), 6·40 (br.s, 2H), 7·75 (s, 6H); MS: $m/e = 340$ (rel. ab. 1·2%), 339 (1·7), 297 (0·6), 253 (5·1), 252 (5·9), 230 (2·2), 229 (17·3), 228 (100·0), 227 (3·0), 226 (10·0), 202 (1·5), 200 (1·4), 114 (1·6), 85 (3·2), 84 (3·2), 83 (2·2), 43 (17·6). UV: $\lambda_{max} = 234$ nm (log $\epsilon = 4{\cdot}90$), 259 (3·84), 267 (3·94), 272 (3·90), 278 (3·89), 288 (3·65), 307 (2·87), 321 (2·77).

b. *From* trans-**76**. From a mixture of 230 mg (1 mmole) of **24** and 230 mg (2 mmole) *trans*-**18**, m.p. 77–78° was obtained as described under (a) 300 mg (0·88 mmole, 88%) of adduct **25**, m.p. 196–198°; NMR ($CDCl_3$): $\tau = 2{\cdot}25$–3·00 (m, 10H), 5·22 (br.s, 2H), 6·43 (br.s, 2H), 7·75 (s, 6H).

From the ether layer was isolated 150 mg of a solid that was crystallized from cyclohexane to furnish 80 mg of *trans*-**18**, m.p. 72–77°.

4,11-*Dihydro*-1,3-*dimethyl*-4,11-o-*benzenoanthra*[2,3-c]-*thiophene* (**26**)

Through a soln of 4·0 g (11·8 mmole) of **25**, m.p. 196–198° in 350 ml MeOH and 50 ml $CHCl_3$, maintained at 55° was bubbled a mixture of H_2S and HCl for 2·5 hr. The mixture was poured into 1 l. 1N NaOH. The chloroform layer was separated and washed with water. After drying and filtering the chloroform layer was concentrated and the residue (4·3 g) crystallized from $CHCl_3$/EtOH to give 3·2 g (9·5 mmole, 80%) white needles, m.p. 230–240°; IR (KBr): 2850, 1420, 1180, 1120, 890, 740 cm^{-1}; NMR ($CDCl_3$): $\tau = 2{\cdot}23$–3·07 (m, 10H), 4·72 (s, 2H), 7·61 (s, 6H); MS: $m/e = 340$ (rel. ab. 9·6%), 339 (32·4), 338 (100·0), 337 (24·2), 324 (13·7), 323 (39·3), 322 (16·9), 321 (11·8), 309 (13·7), 289 (14·2), 280 (14·6), 279 (46·1), 278 (11·4), 228 (13·2), 168 (31·5), 163 (23·3), 162 (27·9), 161 (19·6), 154 (28·3), 85 (47·0), 83 (70·3), 59 (22·4), 47 (16·0).

A small sample was crystallized a few times from abs alcohol to yield the analytically pure sample, m.p. 238–243°: (Found: C, 85·3; H, 5·4; S, 9·6. Calcd. for $C_{24}H_{18}S$: C, 85·17; H, 5·36; S, 9·47%); UV: $\lambda_{max} = 226$ nm sh (log $\epsilon = 4{\cdot}90$), 229 (4·91), 237 (4·88), 249 (4·59), 267 (4·26), 276 (4·08), 289 (3·63), 296 (3·03), 302·5 (2·94), 309·5 (3·22), 315·5 (2·95), 323·5 (3·34).

4,11-*Dihydro*-1,3-*dibromomethyl*-4,11-o-*benzenoanthra*-[2,3-c]*thiophene* (**27**).

To a soln of 2·75 g (8·1 mmole) of **26**, m.p. 230–240° in 60 ml boiling CCl_4 were added 2·95 g (16·5 mmole) NBS and 0·1 g dibenzoylperoxide. After 30 min boiling the red mixture was filtered. The residue was dried to give 1·62 g (16·4 mmole, 99%) succinimide, m.p. 121·5–124·5°. The CCl_4 layer was washed with 1N HCl and water, dried over $CaCl_2$ and concentrated. The yellow residue (4·0 g) was crystallized from light petroleum b.p. 60–80° to afford 3·12 g (6·3 mmole, 78%), of a slightly yellow solid, m.p. 200° (d); IR (KBr): 1220, 1180, 740 cm^{-1}; NMR ($CDCl_3$): 2·25–3·07 (m, 10H), 4·53 (s, 2H), 5·37 (s, 4H); MS: $m/e = 498$ (rel. ab. 9·5%), 496 (16·0), 494 (8·9), 418 (29·3), 417 (100·0), 416 (29·3), 415 (100·0), 337 (24·8), 336 (32·2), 335 (24·8), 323 (13·8), 322 (15·5), 305 (12·0), 304 (15·5), 280 (18·7), 278 (12·5).

4,11-*Dihydro*-1,3-*diacetoxymethyl*-4,11-o-*benzenoanthra*-[2,3-c]*thiophene* (**28**).

A mixture of 2·92 g (5·9 mmole) of **27**, 1·75 g (17·7 mmole) anhyd NaOAc and 15 ml AcOH was heated at 80° for 2 hr. The brown mixture was cooled and poured into a mixture of 15 g ice and 15 g water. The ppt was taken up in ether and the ether soln extracted with three 20 ml portions sat $NaHCO_3$aq and two 50 ml portions water. The resulting ether layer was dried over Na_2SO_4 and concentrated, leaving 2·46 g (5·4 mmole, 92%) yellow solid, m.p. 162–168°; IR (KBr): 1730, 1440, 1370, 1220, 1020, 960, 740 cm^{-1}; NMR ($CDCl_3$): $\tau = 2{\cdot}27$–3·03 (m, 10H), 4·42 (s, 2H), 4·75 (s, 4H), 8·00 (s, 6H); MS: $m/e = 456$ (rel. ab. 11·0%), 455 (34·5), 454 (100·0), 411 (21·3), 396 (12·7), 395 (28·2), 353 (11·7), 352 (36·5), 351 (11·7), 335 (18·2), 334 (16·6), 321 (20·6), 289 (10·5), 228 (17·4), 131 (11·5), 43 (37·2).

4,11-*Dihydro*-4,11-o-*benzenoanthra*[2,3-c]*thiophene*-1,3-*dicarboxylic acid* (29)

To the reaction product of 32 mg Na and 15 ml abs EtOH was added 2·31 g (5·1 mmole) of **28**, m.p. 162–168°. The dark brown mixture was shaken well for 15 min and then set aside for 70 hr. After evaporation of the solvent, the residue was treated with 20 ml EtOH, filtered and the filtrate evaporated to dryness. The brown solid (1·8 g) was stirred with a soln of 1·5 g KOH in 30 ml water at 35° for 4 hr. After one day at room temp the mixture was cooled to 0° and over a period of 4·5 hr 2·33 g (12·2 mmole) finely ground $KMnO_4$ was added. The excess permanganate was destroyed with EtOH and the brown mixture filtered. The residue was boiled twice with 100 ml 2N NaOH and the combined basic layers were acidified with 6N HCl. The ppt was collected and dried, giving 370 mg (0·93 mmole, 18·5%) yellow solid; IR (KBr): 3200, 1680, 1470, 1260, 740 cm^{-1}; NMR (CD_3OD): $\tau =$ 2·22–3·02 (m, 10H), 3·67 (s, 2H); MS: $m/e = 399$ (4·9), 398 (15·0), 382 (4·7), 368 (4·6), 354 (5·1), 353 (6·2), 352 (7·9), 310 (5·7), 309 (12·0), 308 (13·9), 307 (4·5), 265 (4·8), 263 (4·7), 252 (4·3), 228 (19·1), 226 (4·4), 154·5 (4·4), 154 (11·2), 153·5 (4·4), 153 (8·1), 149 (6·9), 131·5 (6·5), 85 (12·1), 71 (19·0), 58 (37·5), 57 (45·8), 45 (55·9), 44 (57·1), 43 (100·0).

4,11-*Dihydro*-4,11-o-*benzenoanthra*[2,3-c]*thiophene* (8)

To a finely ground mixture of 350 mg (0·83 mmole) of **29** and 700 mg Cu-II oxide was added 5 ml quinoline. The mixture was heated at 220° (external temp) until the evolution of gas stopped (4 min). The mixture was then rapidly cooled, filtered and diluted with chloroform. The organic soln was extracted with 1N HCl until basification of the acidic layer did not give visible turbidity. The chloroform layer was then washed with three 50 ml portions of 2N NaOH and two 50 ml portions water. The dried soln was filtered and chromatographed over alumina with benzene. The eluate gave upon concentration 116 mg (0·37 mmole, 43%) white solid, m.p. 285–289°; IR: 890, 840, 780, 750 cm^{-1}; NMR: $\tau =$ 2·23–3·05 (m, 10H), 3·07 (s, 2H), 4·57 (s, 2H); MS: $m/e =$ 312 (rel. ab. 8·7%), 311 (26·4), 310 (100·0), 309 (73·6), 308 (38·0), 276 (7·6), 265 (25·8), 263 (10·4), 228 (2·5), 155 (10·0), 154 (18·7).

A small sample was crystallized a few times from abs EtOH to furnish colourless plates, m.p. 288–291°. (Found: C, 85·0; H, 4·5. Calcd. for $C_{22}H_{14}S$: C, 85·16; H, 4·52%); UV: See Table 4.

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