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THE SYNTHESIS OF A RESOLVED TRIPTYCENE[1]

SPECTROSCOPIC EVIDENCE FOR TRANSANNULAR INTERACTION

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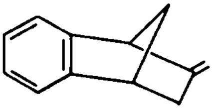
Abstract—The synthesis of optically active 4,11-dihydro-4,11-o-benzenoanthra[2,3-b]thiophene (**3**) is reported. Resolution of **3** was achieved via the dehydroabietylamine salt of the 2-thiophene substituted carboxylic acid (**4**). Desulfurization of optically active **3** furnished optically active 5,12-dihydro-5,12-(13-ethyl)ethanonaphthacene (**6**). Comparison of the CD data of this compound and of **3** led to the conclusion that π-π interaction between all three rings in triptycene systems exists.

INTRODUCTION

THE question of through-space pi-interaction between the nonconjugated aromatic rings in triptycenes has been a matter of considerable interest and controversy.[2-8] From the interpretation of the ESR spectra of triptycene radical cations[2,7] it was concluded that intramolecular electron density transfer exists in this ion. On the other hand, UV spectra of triptycene[5] and substituted triptycenes[3] show only a small bathochromic shift when compared with appropriate model compounds. Calculations indicate[5] that this small bathochromic shift need not necessarily be attributed to inter benzene π-π interactions. Another system where these π-π interactions would be expected are the helicenes,[9,10] where aromatic rings overlap and are forced close together.[11] Nevertheless the data of Groen and Wynberg[9] clearly show that this overcrowding, which must exist, cannot be observed through a study of the UV spectra. This means, that UV spectroscopy is not a sensitive technique for the detection of through space pi-interactions. On the other hand ORD and CD spectra are exceedingly sensitive to perturbations in the neighbourhood of the asymmetric centre.[12] Illustrative of these statements is the work of Mislow and Sandman.[13] These workers compared both the UV and CD spectra of (+)-2-methylene benznorbornene (**1**) and (+)-*exo*-2-benznorbornenol (**2**).



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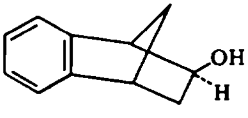

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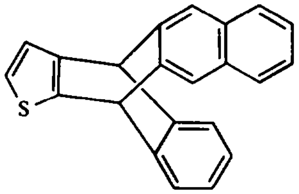
Although the absorption of **1** for the $B_{2u} \leftarrow A_{1g}$ transition at 250–280 nm is intensified only slightly and shifted almost negligibly when compared to **2**, the optical rotatory power (as measured by the molecular ellipticity) of **1** in this spectral region is considerably stronger than that of **2**. Moreover the Cotton effect at 224 nm is attributed to a mixing of ethylenic and benzenoïd states. This is based on a comparison of the intensity of this Cotton effect with the normally low intensity of this effect in the comparable nonhomoconjugated compound **2**. The UV spectra of **1** and **2** do not indicate this π-orbital interaction.

In triptycene systems, similar effects might be operating. It was hoped therefore that the CD and ORD spectra of a resolved triptycene would provide the desired information.

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 an unsubstituted asymmetric triptycene was undertaken.

RESULTS

In an earlier paper[14] we described the synthesis of a triptycene (3) which met the specified requirements of asymmetry.



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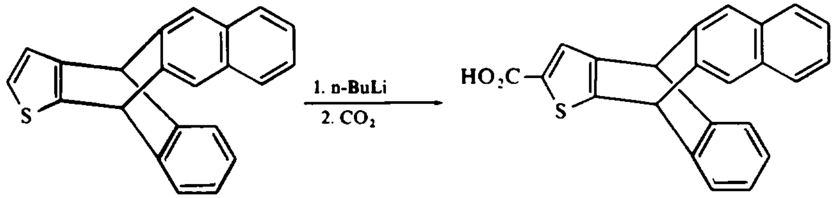
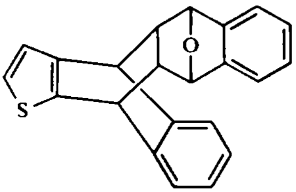
Resolution of 3 following the procedures given by Martin[15] and Wynberg and Groen[16] was not successful (see Exp). Resolution via diastereomer formation was therefore necessary.[17] To achieve this, the molecule must be given a "handle" in order to be able to obtain diastereomeric salts. Since a thiophene-ring is present in the molecule, introduction of a carboxyl group is an obvious choice. The acid 4 was prepared in good yield by the well-known lithiation-carboxylation sequence.[18,*]



3 4

[*] In order to obtain large amounts (up to 10 g) of the carboxylic acid 4 a bulk synthesis of the triptycene (3) was developed. A break-through improvement of our previous described route[14] was the dehydration of adduct 5 with triphenylphosphonium dibromide.



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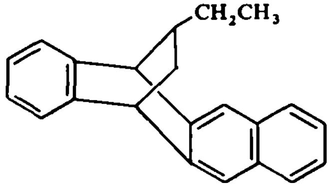
See Ph. D. dissertation of J. de Wit and a forthcoming paper for experimental and mechanistic details.

After the usual number of unsuccessful attempts (using brucine and quinine) resolution of **4** was achieved with dehydroabietylamine.[19]

Optimum conditions were found by applying the method described by Gustafsson.[20] Hydrolysis of the salt after five crystallizations gave 1-acid, $[\alpha]_{405} = -13{\cdot}3$. An IR spectrum of this material was identical with that of racemic **4**. This acid was converted into optically active **3** by decarboxylation with copper II oxide[21] in quinoline. The triptycene, obtained in 77% yield, had $[\alpha]_{365} = +32{\cdot}5$. The identity of this coumpound was proved by its physical constants and by comparing the UV spectrum with that of racemic **3**. No attempts were made to determine the optical purity of this material, mainly because of a lack of enough resolved acid (**4**). In order to be able to compare the properties of optically active **3** with those of a compound with identical optical purity but lacking the typical triptycene structure, optically active **6** was prepared from (+)-**3**.

Desulfurization of (+)-**3** with Ra-Ni (W-7[22]) gave optically active 5,12-dihydro-5,12-(13-ethyl)ethanonaphthacene (**6**) in 50%-yield.



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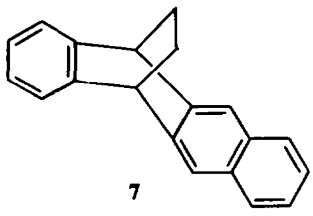

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Structure proof of this compound was carried out on racemic **6**, obtained from reaction between racemic **3** and Ra-Ni in 40%-yield.

The structure of compound **6** was supported by analysis and spectra, of which the UV spectrum was almost identical with that of 5,12-dihydro-5,12-ethanonaphthacene (**7**)[23] (Table 1). The UV spectrum of optically active **6** was exactly the same as that of racemic **6**.

TABLE 1. UV SPECTRA IN CYCLOHEXANE.
sh = shoulder

Compound	λ_{max}	(log ε)						
6	217 sh	(4·60)	259	(3·85)	277·5	(3·90)	305·5	(2·87)
	232·5	(4·93)	267	(3·95)	286·5	(3·68)	317 sh	(2·57)
	236 sh	(4·89)	271	(3·93)	288·5	(3·65)	319·5	(2·90)
7	216 sh	(4·53)	249	(3·72)	271	(3·91)	306	(2·88)
	232	(4·88)	259	(3·80)	278	(3·86)	320	(2·92)
	236 sh	(4·86)	267	(3·92)	289	(3·63)		

DISCUSSION

In Fig 1 the UV and CD spectra of the resolved triptycene **3** are shown. An ORD spectrum was taken of a solution of **3** in cyclohexane. Owing to apparatus instabilities it is difficult to locate the different Cotton bands in the spectrum, so that the spectrum

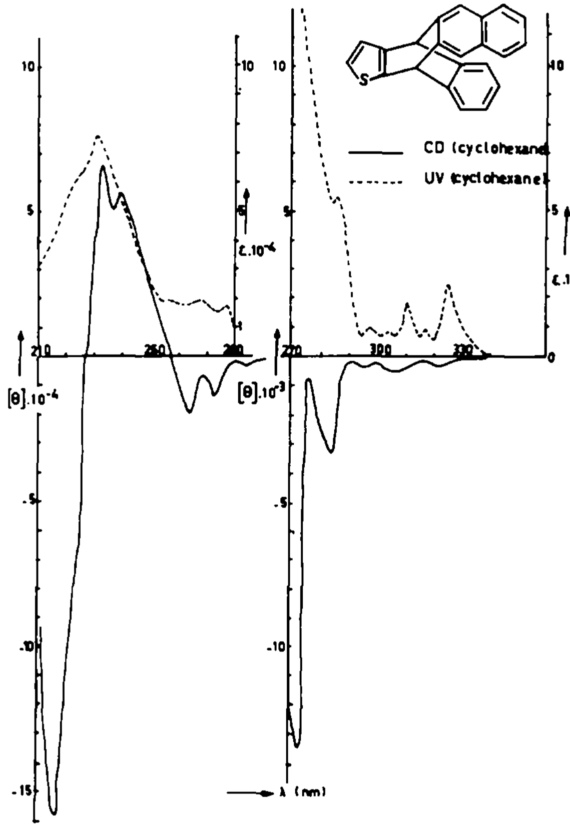


FIG. 1. UV and CD spectra of 4,11-dihydro-4,11-o-benzenoanthra[2,3-b]thiophene (3) in cyclohexane (note the difference in scale left and right).

is not presented. The CD spectrum is much clearer. We see that the α- and p-bands[24] give rise to a negative dichroism whereas the β-band gives a positive dichroism. At short wavelength (217·5 nm) a strong negative dichroism is observed.

The CD and UV spectra of optically active **6** are shown in Fig 2. The concentration of **6** in the solution of which the CD spectrum was taken, was determined with UV spectroscopy.

It can be seen that no dichroism is observable for the α-band and only weak dichroisms for the p- and β-bands, compared to those of optically active **3**. This decrease in molecular ellipticity is not due to the generation of a new asymmetric centre by the desulfurization reaction, because **6a** and **6b** are diastereomers and not enantiomers.[25] If the CD spectra of **3** and **6** (Fig 3) are compared with those of **1** and **2** respectively, striking similarities are noted.

The Cotton effect for the α-band of **6** was not observable whereas **3** exhibits a negative Cotton effect with θ_{max} = 300–400. This is not surprising since the absorptivity of the α-band in **6** is only $\frac{1}{4}$ of that of **3**. The absorption of the p-band of **3** is intensified only by a factor 1·5 when compared to **6** but the intensity of the Cotton effect in this region is enhanced almost 10-fold. Mislow[13] has attributed a similar

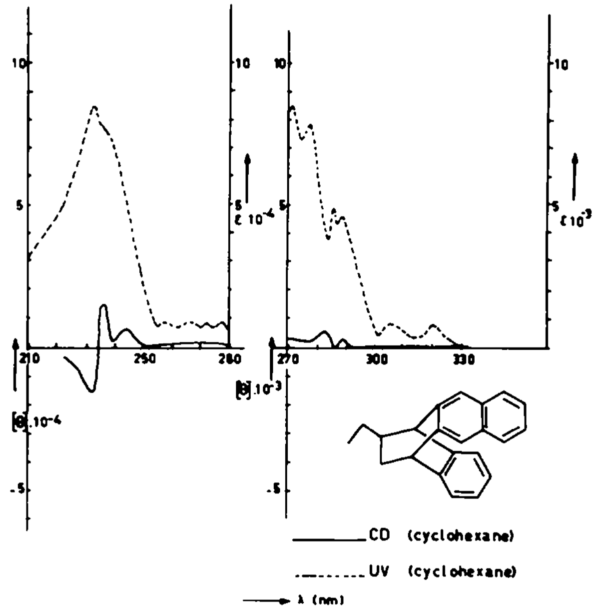
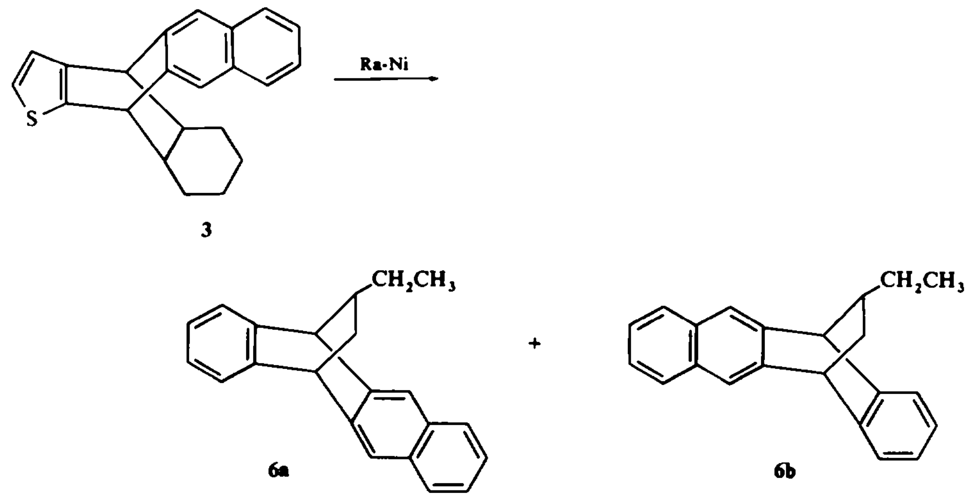


FIG. 2. UV and CD spectra of 5,12-dihydro-5,12-(13-ethyl)ethanonaphthacene (6) in cyclohexane (note the difference in scale left and right).



$$\mathrm{dl} \xrightarrow{\mathrm{RaNi}} \mathrm{dd} + \mathrm{dl} + \mathrm{ld} + \mathrm{ll}$$

$$\mathrm{d(l)} \xrightarrow{\mathrm{RaNi}} \mathrm{dl\,(ll)} + \mathrm{dd\,(ld)}$$

enhancement comparing the 224 nm Cotton effect of **1** and **2** to mixing of ethylenic and benzenoid states.

We therefore ascribe the enhanced Cotton effect to mixing of aromatic states of all three rings. If this conclusion is valid then the CD measurement of **3** has given us new information on π-π interaction in triptycene systems.

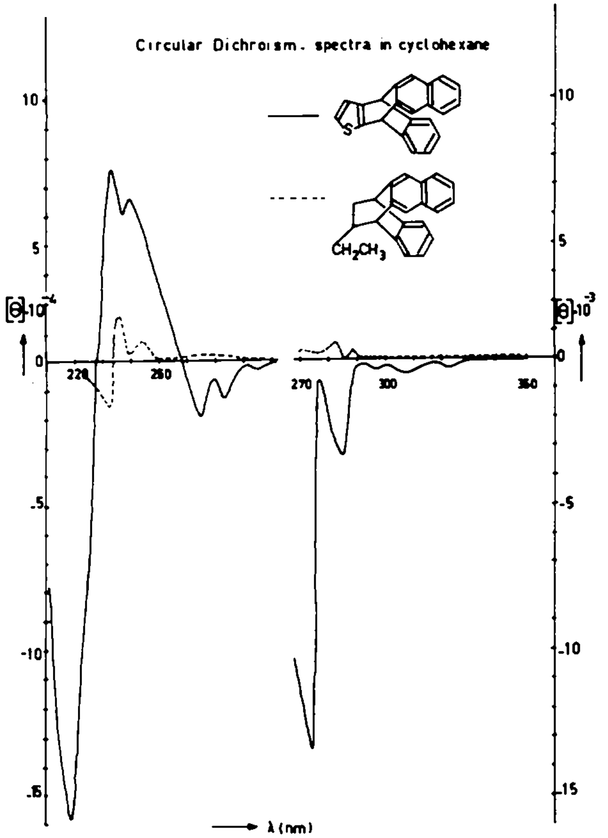


FIG. 3. CD Spectra of 4,11-dihydro-4,11-o-benzenoanthra[2,3-b]thiophene (3) (———) and 5,12-dihydro-5,12-(13-ethyl)ethanonaphthacene (6) (- - - - -) in cyclohexane (note the difference in scale left and right).

EXPERIMENTAL

M.ps were determined on a Reichert hot-stage apparatus and are uncorrected. B.ps are uncorrected. IR spectra were taken on a Unicam SP 200, only significant and/or large peaks are reported. Mass spectra were obtained with an AEI MS 902 instrument; 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 parts per million on the τ-scale. UV spectra were taken of p.a. samples on a Zeiss PMQ II, unless otherwise stated. If not mentioned cyclohexane Uvasol (Merck) was used as a solvent.

Elemental analysis were carried out in the micro-analytical department of this laboratory by Mrs. H. Draaijer, J. Ebels, W. M. Hazenberg and J. E. Vos.

Column chromatography was performed on alumina (neutral, activity 1, Merck A.G.) or silica (B.D.H.) with distilled and dried eluents. TLC was carried out on a small glass plates (2·5 × 5 cm) covered with a thin layer of silica (Merck, 'G'). Distilled and dried eluents were used and the plates were developed with I_2 vapour. Rotations were measured on a Zeiss Lep 005 of solns of the compounds in suitable solvents. The accuracy of the measurements is 0·005°; the error in the specific rotations is approximately 5%.

CD-spectra (in cyclohexane soln) were determined with a Roussel-Jouan Dichrographe II by Mr. M. O. v.d. Meer (Dept. Phys. Chem.).

Attempted resolution of 3 *via crystallization.* A soln of 50 mg of 3 in 10 ml benzene was allowed to stand for 48 hr. After all of the benzene had been evaporated, the crystals obtained (with an average weight of 0·3 mg) proved to be inactive as measured in chloroform soln at 405 nm.

Attempted resolution of **4** *with brucine and quinine.* To a soln of 1·95 g (5·5 mmole) of **4** in 110 ml boiling EtOH was added a soln of 1·30 g (2·75 mmole) brucine-tetrahydrate and the resulting yellow soln was boiled for 30 min. After cooling for one night in a refrigerator (− 25°) the ppt was collected and dried to give 1·96 g of a yellow salt. This salt was crystallized twice from abs EtOH and 3 times from an alcohol-water mixture. The slightly yellow solid (247 mg) was dissolved in 10 ml AcOH and boiled for 2 min. After addition of 25 ml water heating was continued for 5 min and, after cooling, water and ether were added. The water layer was separated and the ether layer extracted with 2N KOH. The yellow basic layer was acidified with 6N HCl to give a slightly yellow ppt, $[\alpha]^{25}_{436} = 0{\cdot}00$ ($c = 0{\cdot}3$, DMSO). The mother liquor from brucine-salt formation was concentrated to give 1·2 g of a yellow solid. This solid was dissolved in 40 ml boiling EtOH; 900 mg (2·75 mmole) of anhyd quinine, m.p. 169–172° (lit. Handbook 174·9°), was added and reflux was maintained for 30 min. During reflux precipitation started. After cooling the mixture for one night in the refrigerator (− 25°) the ppt was collected and dried. The white solid (800 mg) was crystallized twice from EtOH/water to give a few mg of a grey powder.

Resolution of **4** *with dehydroabietylamine*

(a) A soln of 286 mg (1 mmole) of dehydroabietylamine, $[\alpha]^{20}_{578} = +61{\cdot}7$, $c = 3{\cdot}07$, pyridine, (lit.[26] $[\alpha]^{20}_{578} = +56{\cdot}1$, $c = 2{\cdot}4$, pyridine) in 5 ml ether was added to a boiling soln of 354 mg (1 mmole) of **4** in 30 ml ether. The mixture was refluxed for 30 min and cooled overnight at − 25°. The white ppt was collected and dried (500 mg) and crystallized 3 times from EtOH to give 82 mg of an almost white solid. This solid was boiled for 2 hr with 20 ml 2N KOH.[20b] After cooling and washing with ether the basic layer was acidified with 6N HCl; no ppt was formed. The ether layer was concentrated and the residue (80 mg) boiled for 30 min with a 50% AcOH soln. After cooling, water and ether was added. The ether layer was extracted with three 25 ml portions of 2N NaOH and the combined basic layer was acidified with 6N HCl. The ppt was collected and dried to give 26 mg of a cream coloured solid $[\alpha]^{20}_{546} = +11{\cdot}4$, $[\alpha]^{20}_{578} = +9{\cdot}0$ ($c = 1{\cdot}2$, DMSO).

(b) A reaction between 890 mg (2·52 mmole) of **4** and 720 mg (2·52 mmole) of **12** in 200 ml ether afforded 1·1 g of an almost white solid. After 5 crystallizations from EtOH the product (210 mg) was hydrolysed with AcOH and water to give 90 mg of a slightly yellow product, $[\alpha]^{20}_{405} = -13{\cdot}3$, $[\alpha]^{20}_{436} = -10{\cdot}0$, $[\alpha]^{20}_{546} = -1{\cdot}7$, $[\alpha]^{20}_{578} = -1{\cdot}7$ ($c = 0{\cdot}3$, DMSO).

Decarboxylation of optically active acid **4**.

A finely ground mixture of 80 mg (0·23 mmole) of **4** ($[\alpha]^{20}_{405} = -13{\cdot}3°$) and 160 mg copper II oxide was brought into 7 ml quinoline. The mixture was heated at 230° (external temp) until the evolution of CO_2 ceased (3 min). After cooling 75 ml chloroform was added. The filtered mixture was extracted with 2N HCl until basification of the extract did not give visible turbidity. The chloroform layer was then extracted with 100 ml of 2N KOH and with 100 ml water and then dried over $CaCl_2$. The red coloured chloroform layer was filtered and concentrated and the residue chromatographed with benzene/hexane (1):(1) over alumina. The eluate was concentrated, leaving 54 mg (0·17 mmole, 77%) of a white solid, $[\alpha]^{20}_{578} = +5{\cdot}8$, $[\alpha]^{20}_{546} = +7{\cdot}2$, $[\alpha]^{20}_{436} = +16{\cdot}4$, $[\alpha]^{20}_{405} = +21{\cdot}9$, $[\alpha]^{20}_{365} = +32{\cdot}5$ ($c = 1{\cdot}8$, chloroform).

The solid was crystallized 3 times from abs EtOH to give 37 mg of white needles, m.p. 268–270°. UV (Cary 15): $\lambda_{max} = 226$ nm ($\log \varepsilon = 4{\cdot}77$), 232·5 (4·86), 250 sh (4·32), 258·5(sh) (4·30), 270 (4·34), 278·5 (4·28), 287·5 (3·79), 298·5 (3·02), 305 (2·96), 312 (3·29), 318 (2·99), 325·5 (3·43). CD (cyclohexane): $[\theta]_{322{\cdot}5} = -330$, $[\theta]_{310} = -400$, $[\theta]_{297{\cdot}5} = -330$, $[\theta]_{285} = -3300$, $[\theta]_{273{\cdot}5} = -13{\cdot}400$, $[\theta]_{265} = -19{\cdot}200$, $[\theta]_{240} = +56{\cdot}000$, $[\theta]_{234} = 66{\cdot}000$, $[\theta]_{217{\cdot}5} = -158{\cdot}000$.

5,12-*Dihydro*-5,12-(13-*ethyl*)*ethanonaphthacene* **6**.

A mixture of 214 mg (0·69 mmole) of **3**, m.p. 278–280°, 5 g of Ra-Ni W7[22] and 150 ml of abs EtOH was refluxed for 5 hr and stirred with a vibromixer. The cooled mixture was transferred to a Soxhlett-thimble and -apparatus and extracted for 24 hr. The extract was concentrated, leaving 280 mg of a yellow oil. The oil was dissolved in hexane and the soln cooled at − 70° for 2 hr. The ppt (60 mg) was filtered and the filtrate chromatographed over alumina with benzene/hexane (1):(1). The eluate gave upon concentrating 87 mg (0·27 mmole, 40%) of a colourless oil. NMR ($CDCl_3$): $\tau = 2{\cdot}23$–$3{\cdot}05$ (m, 10H), 5·77 (m, 2H), 7·66–9·27 (m, 8H). IR (liquid): 3050, 2900, 1500, 1470, 1440, 1250, 1080, 1020, 880, 800, 730 cm^{-1}. Ms: m/e = 284 (rel. ab. 3·1%), 282 (2·9), 230 (2·4), 229 (22·2), 228 (100·0), 227 (4·5), 226 (10·7), 225 (2·2), 224 (3·0), 202 (2·9), 200 (2·6), 114 (6·0), 112 (2·5), 101 (2·0), 83 (3·0).

An analytically pure sample was prepared by repeated chromatography. Evaporation of the eluate gave a colourless oil which solidified on standing and had m.p. 83–103°. (Found: C, 93·0; H, 7·2. Calc for $C_{22}H_{20}$: C, 92·91; H, 7·09%). UV: see Table 1. UV (Cary 15): λ_{max} = 320·5 nm (log ε = 2·92), 317·5 sh (2·52), 307 (2·90), 289·5 (3·68), 278·5 (3·90), 272·5 (3·94), 268 (3·96), 260 (3·86), 238 sh (4·86), 234 (4·94), 218·5 (4·63).

Optically active 5,12-*dihydro*-5,12-(13-*ethyl*)*ethanonaphthacene* (6).

A mixture of 25·60 mg of 3, $[\alpha]_{365}$ = + 32·5°, m.p. 278–280°, 0·5 g Ra-Ni W7[22] and 150 ml EtOH was refluxed for 6 hr and stirred with a vibromixer. The mixture was cooled and filtered through a thimble into a Soxhlett-apparatus. The excess of catalyst was extracted with EtOH for 15 hr. The residue was concentrated, leaving a yellow oil that consisted of both product and starting material (TLC, cyclohexane). The oil was dissolved in 20 ml of boiling EtOH and stirred and refluxed for 6 hr with a fresh portion of Ra-Ni (1 g). Work-up as described above, followed by chromatographical purification gave 11·65 mg (0·41 mmole, 50%) of a colourless oil. UV (Cary 15): λ_{max} = 218, 233·5, 237 (sh), 260, 268·5, 272·5, 279, 290, 306·5, 317, 320 (see also Fig 3). CD: $[\theta]_{288\cdot5}$ = + 300, $[\theta]_{282\cdot5}$ = + 630, $[\theta]_{244}$ = + 6600, $[\theta]_{236}$ = + 16·500, $[\theta]_{232\cdot5}$ = − 16·500.

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