One-pot Synthesis of 5,11-Dihydro-5,11[1′,2′]-benzenocyclohepta[*b*]naphthalenylium Tetrafluoroborate(1 −) as a Precursor for a Study on the Isomerisation of Dihydro-5,11[1′,2′]-benzeno-5*H*-cyclohepta[*b*]naphthalenes

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One-pot Synthesis of 5,11-Dihydro-5,11[1′,2′]-benzenocyclohepta[*b*]naphthalenylium Tetrafluoroborate(1 −) as a Precursor for a Study on the Isomerisation of Dihydro-5,11[1′,2′]-benzeno-5*H*-cyclohepta[*b*]naphthalenes

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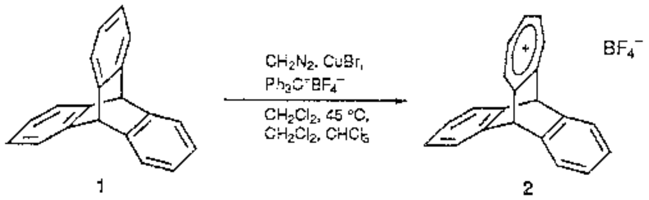
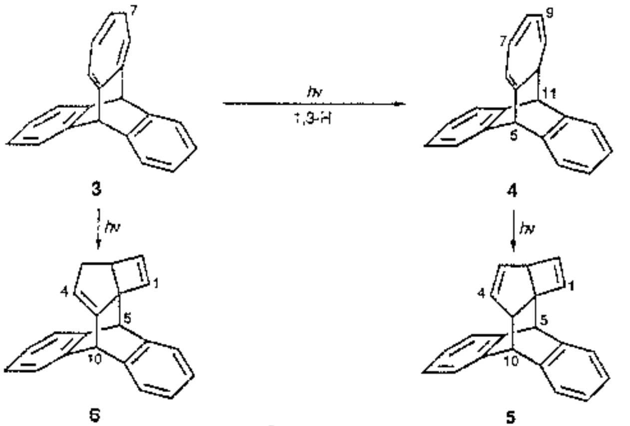
5, 11 - Dihydro - 5, 11 [1′, 2′] benzenocyclohepta [*b*] naphthalenylium tetrafluoroborate(1 −) (**2**) has attracted considerable attention in recent years in studies of intramolecular charge-transfer between donor and acceptor components fixed in rigid spatial arrangements.[1-3] It was first synthesized by Nakazawa and Murata in 1977[2] and then by Butler and Gupta in 1978.[3] The Japanese group prepared the compound *via* a twelve-step synthesis starting from commercially available tropolone involving cycloaddition of 4,5-didehydrotropone and anthracene followed by reduction, elimination and final abstraction of a hydride ion. The overall yield of this sequence was below 1%.[2] The Canadian group used a six-step synthesis which involved cycloaddition of maleic anhydride and anthracene, conversion of the cycloadduct into 9,10-dihydro-11,12-dimethylene-9,10-ethanoanthracene, cycloaddition onto cyclopropene, subsequent dehydration with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and finally abstraction of hydride. The overall yield of this sequence was 32%.[3] During a study on the isomerisation of dihydro-5,11[1′,2′]-benzeno-5*H*-cyclohepta[*b*]naphthalenes discussed below, a convenient one-pot synthesis of **2** has been developed which affords this compound on, for example, a 5 g scale starting from commercially available triptycene (**1**). The reaction involves a copper(I) bromide-catalysed ring enlargement by diazomethane in boiling methylene dichloride and subsequent conversion with triphenylmethylium tetrafluoroborate as shown in Scheme 1.



Scheme 1

The title compound **2** was prepared in a yield of 34% (based on consumed triptycene). The full paper presents the complete structural assignment and spectroscopic data of this substance. Moreover, it describes the direct photolysis of 7,11-dihydro-5,11[1′,2′]benzeno-5*H*-cyclohepta[*b*]naphthalene (**3**) which affords the 5a,11-dihydro isomer (**4**) as the primary photoproduct, with prolonged photolysis affording 2a,4a,5,10-tetrahydro-5,10[1′,2′]-benzeno-5*H*-cyclobuta-[2,3]cyclopenta[1,2-*b*]naphthalene (**5**) and its 2a,3,5,10-tetrahydro isomer (**6**) resulting from intramolecular [2 + 2] photocyclisation of the two cycloheptatrienes. The corresponding deuterated compound $[^2H_1]$-**3** upon direct photolysis afforded $[^2H_1]$-**4** wherein the deuterium is concentrated at the 7 and 9 positions of the cycloheptatriene moiety.



Scheme 2

The isomerisation of **3** and **4** is shown in Scheme 2. Under direct irradiation at 254 nm, **3** in Et_2O underwent facile photoisomerisation to afford **4** as the main photoproduct, the non-photochemical synthesis and spectroscopic data of which have already been published.[8] On prolonged irradiation, whereby a photostationary state between **3** and **4** is established, two further photoproducts, **5** and **6**, were obtained in minor amounts in the ratio 2:1. These photoisomers were inseparable under HPLC conditions. However, their structures were established by analysis of their ^{1}H NMR spectra and by the results of nuclear magnetic double resonance experiments.

Techniques used: Medium-scale diazomethane conversion, direct irradiation, HPLC separation, ^{1}H NMR, ^{13}C NMR, IR, MS, UV, double resonance experiments, deuterium labelling

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Study on the Isomerisation of 9,10-Dihydro-9,10-(X',X'-cyclohepta-trieno)anthracenes

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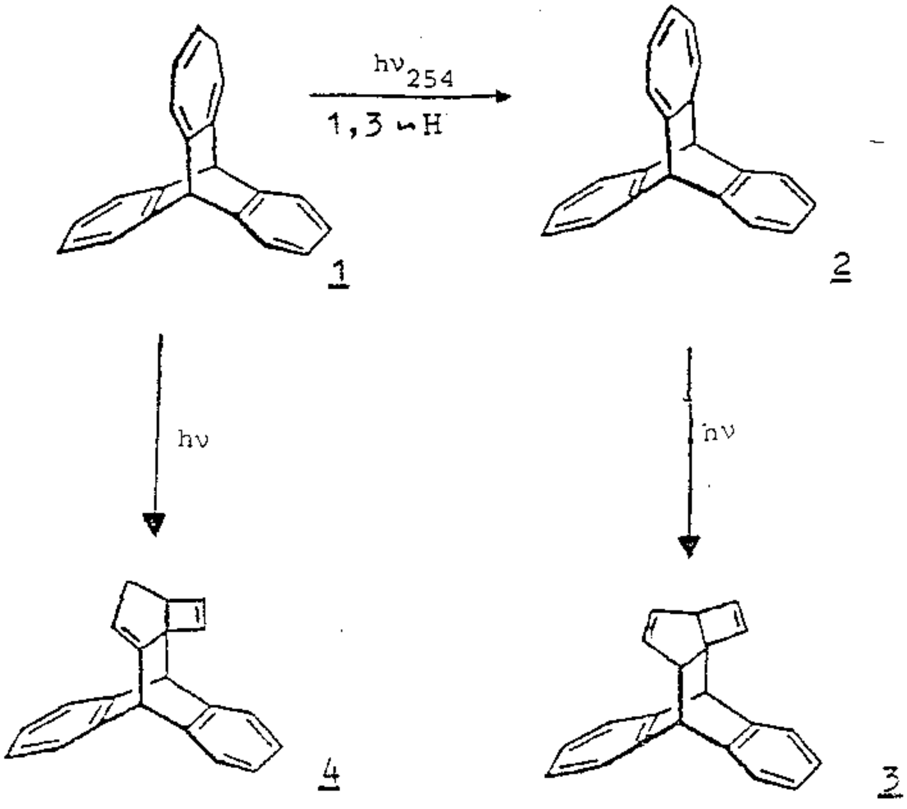
Direct photolysis of 9,10-dihydro-9,10-(2',3'-cycloheptatrieno)-anthracene **1** afforded 9,10-dihydro-9,10-(1',7'-cycloheptatrieno)-anthracene **2** as primary photoproduct. The prolonging of the photolysis afforded 9,10-dihydro-9,10-(6',7'-bicyclo$[3.2.0^{3',7'}]$-hepta-1',4'-dieno)anthracene **3** and 9,10-dihydro-9,10-(6',7'-bicyclo-$[3.2.0^{3',7'}]$-hepta-1',5'-dieno)anthracene **4** resulting from intra-molecular [2+2]-photocyclisation of the two cycloheptatrienes. The corresponding deuterated compound **1**$_{d1}$ upon direct photolysis af-forded **2**$_{d1}$ wherein the deuterium is concentrated at the 3 and 5 position of the cycloheptatriene moiety. Compound **1** was stable upon heating at 130°C for 24 h.

9,10-Dihydro-9,10-(9 X',10 X'-cycloheptatrieno)anthracenes are representatives of a bichromophoric molecules's class i.e. of molecules comprising two chromophores not directly conjugated with one another. Said molecules, from the theoretical point of view, may photochemically react either as typical cycloheptatriene derivatives,[1] or via a di-π-methane-rearangement as a dibenzobarrelene derivative[2] or via a carbene intermediate[3] or by an interaction of the two type of chromophores.[4]

The isomerisation of 1 is shown in the scheme.



1 under direct 254 nm-irradiation in Et_2O underwent facile photoisomerisation to afford **2** as the main photoproduct, the nonphotochemical synthesis and spectroscopic data of which have been already published.[5]

On prolonged irradiation two further photoproducts 3 and 4 are obtained in minor amounts being produced in the ratio 2 : 1 which are unseparable under HPLC-conditions. However, the structure of these photoisomers was established by analysis of its ^{1}H-NMR spectra and by the results of nuclear magnetic double resonance experiments.

The aliphatic portion of the ^{1}H-NMR spectrum of **3** consists of a doublet of doublets at 2.79 ppm, a complex signal at 3.10 ppm, a bridgehead singlet at 4.25 ppm and a bridgehead doublet at 4.40 ppm; the olefinic portion consists of two singlets at 5.58 ppm, a dublet at 6.05 ppm and a dublet of dublets at 6.33 ppm. Thus, **3** is the intramolecular [2 + 2]-photocyclization product of photoisomer

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The aliphatic portion of the ^{1}H-NMR spectrum of **4** consists of a doublet of doublets at 2.30 ppm, a dublet at 2.30 ppm, a broad doublet at 2,98 ppm, a bridgehead singlet at 4.37 ppm and a bridgehead singlet at 4.88 ppm; the olefinic portion consists of a triplet at 5.40 ppm, a doublet of dublets at 5.63 ppm and a dublet at 6.26 ppm. Thus, **4** is the intramolecular [2 + 2]-photocyclization product of **1**, i.e. 9,10-dihydro-9,10-(6',7'-bicyclo-[3.2.0$^{3',7'}$]hepta-1',5'-dieno)anthracene.

The direct photolysis of **1**$_{d1}$ afforded **2**$_{d1}$ having a 1H-NMR spectrum which is almost similar to the spectrum of 2. However, as could be estimated from the design of the broad signals of the olefinic hydrogens of said compound in contrast to the less broad signals of the methylene group and the sharp signals of the bridgeheadprotons this photoproduct is obtained by 1,3-sigmatropic shifts wherein the deuterium is mainly concentrated at the positions 5 and 3.

To get more informations on the above isomerisation thermolysis of **1** has been performed for 24 h at 130 C, however, no thermal isomerisation could be detected. Likewise, T. Mukai et al showed that **2** does not isomerize even at 150 C for 40 h.[5]

The synthesis of the starting material 9,10-dihydro-9,10-(2',3'-cycloheptatrieno)anthracene **1** by a multistep-approach is published elsewhere.[6,7] The independent synthesis of 9,10-dihydro-9,10-(1',7'-cycloheptatrieno)anthracene **2**, the primary photoproduct of this study, is also published.[5]

The melting points are corrected and were taken using a Tottoli apparatus. ^{1}H-NMR spectra were recorded on a Bruker WP-80 (80 MHz) and ^{13}C-NMR spectra were recorded on a Bruker WH 90 (22.64 MHz). Mass spectra were measured on a Varian CH-5. IR-spectra were recorded on a Perkin-Elmer 257. The UV-spectrum was recorded on a

Perkin Elmer 402. The solvents were dried before use. The synthesis of 9,10-dihydro-9,10-(*o*-tropylio)anthracene tetrafluoroborate is published elsewhere.[6,7,8]

9,10-dihydro-9,10-(2',3'-cycloheptatrieno)anthracene (1):

To 9,10-dihydro-9,10-(o-tropylio)anthracene tetrafluoroborate (0.913 g, 2.57 mmol) dissolved in dry MeCN (300 ml) sodium borohydride (0.29 g, 7.7 mmol) was added and the reaction mixture was stirred for about 120 min. The pale yellow emulsion was then concentrated *in vacuo* to about 10 ml, and water (200 ml) was added to the residue. The aqueous phase was extracted six times with pentane and after drying (sodium sulfate), the solvent was removed from the combined organic phases *in vacuo*.

Recristallisation from MeOH afforded compound **1** as colorless cristalls (yield: 390 mg (56.4 %)).

mp: 202°C (Lit.[6] 196°C-199°C, Lit.[7] 202°C).

^{1}H-NMR (tetradeuteriomethanol): δ = 2.24 (t, 2H, J = 7.2 Hz), 4.94 (s, 1H), 4.98 (s, 1H), 5,20 (dt, 1 H, J = 6.3 and 9.6 Hz), 5.41 (t, 1H, J = 6.3 Hz), 5,94 (dd, 1H, J = 6.1 and 9.6 Hz), 6.55 (d, 1H, J = 6.1 Hz), 6.85-7.60 ppm (complex, 8H).

^{13}C-NMR (deuteriochloroform): δ = 27.55 (t, 1C, J = 128.0 Hz), 55.11 (d, 1C, J = 140.9 Hz), 56.62 (d, 1C, J = 139.1 Hz), 113.80 (d, 1C, J = 156.3 Hz), 117.96 (d, 2C, J = 155.7 Hz), 122.21 (d, 1C, J = 156.3 Hz), 123.21 (d, 2C, J = 160.0 Hz), 124.60 (d, 2C, J = 159.0 Hz), 125.56 (d, 2C, J = 159.0 Hz), 125.82 (d, 2C, J = 160.0 Hz), 126.68 (d, 2C, J = 159.0 Hz), 143.57 (s, 1C), 144.10 (s, 4C), 144.35 ppm (s, 1C).

IR (KBr): 3050 (s), 3000 (s), 2980 (s), 1470, 1460, 1380, 1320, 1310, 1205, 1200, 1165, 1140, 1120, 1030, 935, 900, 885, 840, 810, 790, 770 (s), 765 (s), 740 (s), 720 (s), 700 (s), 655 cm^{-1} (s).
MS, m/z (relative intensity): 269 (22, $M^{+}+1$), 268 (100, M^{+}), 267 (57), 265 (29), 254 (18), 253 (65, $C_{20}H_{13}^{+}$), 252 (53), 239 (16), 178 (20), 126 (28).
UV (MeCN): 274 (3.62), 279 nm (3.74).

9,10-dihydro-9,10-(7'-deuterio-2',3'-cycloheptatrieno)anthracene (1_{d1}):

This compound was synthesized in analogy to the undeuterated compound **1**, using sodium borodeuteride (0.35 g, 8.4 mmol) and 9,10-dihydro-9,10-(o-tropylio)anthracene tetrafluoroborate (1.5 g, 4.2 mmol) as starting materials affording the deuterated compound in a yield of 766 mg (68.1 %) after cristallisation from MeOH. mp: 202 °C
^{1}H-NMR (deuteriochloroform): δ = 2.20 (br. t, 1H, J = 6.4 Hz), 4.92 (s, 1H), 4.95 (s, 1H), 5,17 (dd, 1 H, J = 6.5 and 9.8 Hz), 5.40 (d, 1H, J = 6.5 Hz), 5,96 (dd, 1H, J = 6.0 and 9.8 Hz), 6.54 (d, 1H, J = 6.0 Hz), 6.85-7.40 ppm (complex, 8H).
^{13}C-NMR (deuteriochloroform): δ = 27.21 (t, $1C_{HD}$), 55.15 (d, 1C), 56.66 (d, 1C), 113.71 (d, 1C), 117.86 (d, 2C), 122.72 (d, 1C), 123.20 (d, 2C), 124.55 (d, 2C), 125.52 (d, 2C), 125.85 (d, 2C), 126.70 (d, 2C), 143.64 (s, 1C), 144.15 (s, 4C), 144.50 ppm (s, 1C).
MS (degree of deuteration): d_0 = 11.4%, d_1 = 87.8%, d_2=0.8%

9,10-dihydro-9,10-(1',7'-cycloheptatrieno)anthracene (2):

A solution of **1** (100 mg, 0.37 mmol) in dry Et_2O (800 ml) was irradiated in a quartz vessel using a Rayonet-Photochemical Reactor with 16 RPR 2537 phosphor lamps. The solution was purged with dry nitrogene prior and during the irradiation and the reaction heat was removed by tap water cooling. After 30 minutes 84 % of the starting material was consumed which was monitored by reversed phase HPLC. The solvent was removed *in vacuo*, the residue dissolved in 20 ml hexane and eluted over a silicagel column and the eluent containing the reaction mixture after again removing the solvent was separated by semipreparative reversed phase HPLC (column: C-18 on lichrosorb Si 100, 10 µm, 150 mm 15.5 mm i. d.; mobile phase $MeOH/H_2O=82/18$).

Three fractions were collected each of which were extracted with pentane yielding 52 mg (52 %) of compound 2 from the second fraction which after recristallisation from pentane has a mp of 136°C (Lit.[5] 136°C).

^{1}H-NMR (deuteriochloroform): δ = 2.48 (m, 1H), 4.56 (d, 1H, J = 3.0 Hz), 4.77 (dd, 1H, J = 4.0 and 9.5 Hz), 4.88 (s, 1H), 5,98 (complex, 1H), 6.29 (complex, 3H), 7.05-7.50 ppm (complex, 8H).

Double resonance experiments: irradiation at 4.77 ppm let to decoupling at 2.48 ppm (into a dublett) and at 5.98 ppm (into a dd); irradiation at 5.98 ppm let to decoupling at 2.48 ppm (into a dd) and at 4.77 ppm (into a dublett).

^{13}C-NMR (deuteriochloroform): δ = 43.34 (d, 1C), 49.04 (d, 1C), 53.95 (d, 1C), 117.82 (d, 1C), 123.00 (d, 1C), 123.55 (d, 1C), 123.91 (d, 1C), 125.43 (d, 1C), 125.64 (d, 1C), 125.73 (d, 1C), 125.82 (d, 1C), 126.00 (d, 1C), 126.27 (d, 1C), 126.70 (d, 1C), 128.34 (d, 1C), 129.73 (d, 1C), 142.13 (s, 1C), 143.32 (s, 1C), 143.93 (s, 1C), 145.05 ppm (s, 2C).

IR (KBr): 3030 (s), 3000 (s), 2850 (s), 1750-1560, 1550, 1485, 1470 (s), 1460 (s), 1390 (s), 1275, 1170, 1120, 1030, 820, 815, 760 (s), 750 (s), 730 (s), 710 (s), 645 cm^{-1} (s).

MS, m/z (relative intensity): 269 (19, M^{++1}), 268 (22, M^{+}), 267 (26), 265 (15), 253 (14, $C_{20}H_{13}^{+}$), 252 (13), 191 (18), 179 (15), 178 (100, $C_{14}H_{10}^{+}$), 90 (16).

9,10-Dihydro-9,10-(6',7'-bicyclo[3.2.$0^{3',7'}$]hepta-1',4'-dieno)-anthracene (3) and

9,10-Dihydro-9,10-(6',7'-bicyclo[3.2.$0^{3',7'}$]hepta-1',5'-dieno)-anthracene (4)

The photolysis of **1** (100 mg) described above for the synthesis of **2** has been repeated 4 times for about 40 minutes and the crude reaction mixture after eluation was separated into three fractions using a tetranitrofluorenone coated reversed-phase column (2 columns, one behind the other, tetranitrofluorenone on Lichrosorb Si 100, 10 µm, 150 mm, 15.5 mm i. d.; mobile phase: MeOH/H_2O:96/4). The extraction of the third fraction with pentane yielding white cristalls of a unseparable mixture of 67 % **3** and 33 % **4** (10 mg, 2.5 %) the weight amounts and the structure of which is determined by ^1H-NMR and double-resonance studies.

Compound **3**:

^1H-NMR (deuteriochloroform): δ= 2.79 (dd, 1H, J = 2.7 and 4.0 Hz), 3.10 (complex, 1 H), 4.25 (s, 1H), 4.40 (d, 1H, J = 2.7 Hz), 5.58 (s, 2H), 6.05 (d, 1H, J = 2.68 Hz), 6.33 (dd, 1H, J = 2.68 and 0.5 Hz) and 6.95 - 7.90 ppm (complex, 8H).

Double resonance experiments: irradiation at 2.79 ppm let to decoupling at 4.40 ppm (into a singlet), irradiation at 3.10 ppm let to decoupling at 6.33 ppm (into a doublet), irradiation at 4.40

ppm let to decoupling at 2.79 ppm (into a doublet), irradiation at 6.05 ppm let to decoupling at 6.33 ppm (into a doublet) and irradiation at 6.33 ppm let to decoupling at 6.05 ppm (into a singlet).

Compound **4**:

^{1}H-NMR (deuteriochloroform): δ = 2.25 (dd, 1H, J = 2.0 and 4.5 Hz), 2.30 (d, 1H, J = 2.6 Hz), 2.98 (br. d, 1H, J = 2.70 Hz), 4.37 (s, 1H), 4.88 (s, 1H), 5.40 (t, 1H, J = 2.6 Hz), 5.63 (dd, 1H, J = 2.72 and 2,70 Hz), 6.26 (d, 1H, J = 2.72 Hz) and 6.95 to 7.90 ppm (complex, 8H).

Double resonance experiments: irradiation at 2.25 or 2.30 ppm, respectively, let to decoupling at 2.98 ppm (into a singlet) and at 5.40 ppm (into a singlet), irradiation at 2.98 ppm let to decoupling at 5.63 ppm (into a doublet), irradiation at 5.40 ppm let to decoupling at 2.25 ppm (into a doublet) and at 2.30 ppm (into a doublet) and irradiation at 5.63 ppm let to decoupling at 2.98 ppm (into a doublet) and at 6.26 ppm (into a singlet).

Compounds **3** and **4**:

MS, m/z (relative intensity): 269 (13, M^{++1}), 268 (66, M^+), 267 (39), 265 (16), 253 (29, $C_{20}H_{13}^+$), 252 (25), 239 (13), 179 (29), 178 (100, $C_{14}H_{10}^+$), 126(13).

UV (MeOH): 278 (2.86), 254 (3.04), 209 nm (4.00).

Direct photolysis of 9,10-dihydro-9,10-(7'-deuterio-2',3'-cycloheptatrieno)anthracene (1_{d1}):

A solution of **1_{d1}** (100 mg; 0.37 mmol) in Et_2O (800 ml) was photolyzed as described above for the conversion of **1** into **2**. Purification and separation of the second fraction of the photolyzed product compound **2d** as colourless cristalls (44 mg) shown to be

9,10-dihydro-9,10-(X^{3,5}-deuterio-1'.7'-cycloheptatrieno)anthracene) by ^{1}H-NMR evaluation.

^{1}H-NMR (deuteriochloroform): The chemical shifts are almost identical with those of the parent compound **2**. However, as could be shown by comparing the values of the two bridgehead hydrogens and of the methine poroton with those of the cycloheptatriene hydrogens, the deuterium absorption has been mainly distributed at the positions 3 and 5 of the cycloheptatriene moiety.

MS (degree of deuteration): d_0 = 10.0 %, d_1 =88.2 %, d_2 = 1.8 %.

Thermolysis of 1:

A solution of 1 (20 mg) in o-dichlorobenzene (50 ml) was refluxed for 24 h at 130°C. After recovery of the substrate from the solvent a ^{1}H-NMR spectrum of this product revealed that it still only consists of pure **5**.

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