Dipyreno- and diperyleno-anthracenes from glyoxylic Perkin reactions

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SUPPLEMENTARY INFORMATION

Published Perkin reactions mentioned

Archetypal Perkin reactions involving either phenylglyoxylic acid or 1-bromo-2-naphtylacetic acid, with reported yields and reaction times in refluxing Ac₂O.¹⁰,¹⁷,¹⁸

Single crystal X-ray diffraction

Structure of tetraethyl 2,5-dibromo-1,4-phenylenebis((1-pyrenyl)maleate) 9a in the crystal at 120 K. Thermal ellipsoids for non-hydrogen atoms are depicted at 50 % probability level (H white, C grey, O red, Br brown).

Packing of 9a molecules along the c axis. Thermal ellipsoids for non-hydrogen atoms are depicted at 50 % probability level (C grey, O red, Br brown). Hydrogen atoms are omitted for clarity.

The crystallographic data were collected with a Bruker APEX II diffractometer, equipped with a graphite monochromator centred on the path of MoKα radiation. A single crystal of 9a, made by slow diffusion of methanol into a DCM solution, was coated with Paratone-N oil and mounted on a fiber loop, followed by data collection at 120 K. The program SAINT was used to integrate the data, which was thereafter corrected using SADABS. The structure was solved using SHELXS-97 and refined by a full-matrix least-squares method on F² using SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions using suitable riding models. The CIF file has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 941140.

Syntheses

2,5-Dibromophenylene-1,4-diaceatic acid 4

With ice bath cooling, conc. sulfuric acid (800g) is cautiously added to water (400g) in a 2L flask. Once the mixture has cooled back down to room temperature, phenylene-1,4-diaceatic acid 3 (126.2g, 194.2 g/mol, 650mmol) is added with stirring, followed by N-bromo-succinimide (231.4g, 178.0 g/mol, 1.30mol), and the resulting suspension is stirred at room temperature for 16h. The suspension is added with stirring to an ice/water mixture (2L), the raw product is filtered off with a large glass filter, washed on the filter with water, oven-dried and recrystallised twice from THF to yield 66.1g of product. The majority of the also formed 2,3-dibromo-phenylene-1,4-diacetic acid (poorly soluble in acetone, not isolated pure) is eliminated from the evaporation residue of the THF mother liquors by crystallisation from ethyl acetone. A further crop of 43.7g of the major 2,5-dibromo isomer (poorly soluble in acetone) is then obtained from the evaporation residue of the ethyl acetate mother liquors by boiling in acetone followed by hot filtration. Combined yield: 99.8g (284mmol, 352.0 g/mol, 44%) of colourless crystals.

Ethyl pyrenyl-1-glyoxylate 5

A solution of pyrene 1 (101.2g, 202.3g/mol, 0.50mol) and ethyl chloroglyoxylylate (75.0g, 136.5g/mol, 0.55mol) in DCM (500mL) is cautiously poured at 0°C into a well stirred slurry of zirconium chloroglyoxylate (75.0g, 136.5g/mol, 0.55mol) in DCM (500mL) in a 2L flask. More DCM (1L) is cautiously poured at 0°C into a well stirred slurry of zirconium tetrachloride (140g, 233.0g/mol, 0.60mol) in DCM (500mL) in a 2L flask. More DCM (1L) is added and the blue mixture is stirred at room temperature for 16h, and then poured into a stirred mixture of ice and 5% aqueous hydrochloric acid (1L). The phases are separated, the organic phase is dried with sodium sulphate, the solvent is evaporated at 50°C, and the product is purified by precipitation from ethyl acetate solution (300mL) with absolute ethanol (900mL). Yield: 132.2g (349.8799; found 349.8799). Mp: 257-267°C (accompanied by sublimation)

FD-HRMS (m/z): M⁺ Calcd for C₁₀H₁₄Br₂O₄ 349.8789; found 349.8799.

M: 257-267°C (accompanied by sublimation)
Pyrenyl-1-glyoxylic acid 6
Ethyl pyrenyl-1-glyoxylate 5 (30.2g, 302.3g/mol, 100mmol) is dissolved with stirring at reflux in ethanol (300mL). A solution of sodium bicarbonate (30g, 84.0g/mol, 357mmol) in water (300mL) is added, whereupon the ester precipitates partially, and the mixture is refluxed for 3h, whereby the reaction mixture becomes a homogeneous solution. The solution is poured onto a mixture of ice and 5% aqueous hydrochloric acid, and the heterogeneous mixture is refluxed for 20h. The mixture is added and stirring at reflux is continued under exclusion of moisture for 3h. Then a solution of DBU (5.0g, 152.2mmol, 33mmol), 1-bromobutane (9.0g, 137.0g/mol, 66mmol) and butanol (7.4g, 74.1g/mol, 100mmol) in dioxane (30mL) is added and stirring at reflux is continued under exclusion of moisture for 16h. The reaction mixture is poured into methanol (1L), whereupon the product crystallises on standing overnight. The yellow precipitate is filtered off and purified by column chromatography in chloroform on silica and recrystallisation from butanol. Yield: 2.68g (1088.9g/mol, 2.46mmol, 74%).

1H-NMR (CDCl3, 400MHz): δ = 9.20-7.25 (m, 18H), 7.25-6.50 (m, 2H), 4.75-2.90 (m, 8H), 1.51 (quint, 7Hz, 4H), 1.16 (sext, 7Hz, 4H) 0.73 (t, 7Hz, 6H), 2.10-0.10 (m, 14H) ppm.
FD-HRMS (m/z): M+ Calcld for C8H8Br2O8 986.1234; found 986.1237.

Mp.: 199-205°C

Tetraethyl 2,5-dibromo-1,4-phenylenebis((1-pyrenyl)maleate) 9a
2,5-Dibromophenylene-1,4-diacetic acid 4 (1.76g, 352.0g/mol, 5mmol), pyrenyl-1-glyoxylic acid 6 (3.29g, 274.3g/mol, 12mmol), triethylamine (5.05g, 101.2g/mol, 50mmol) and acetic anhydride (10.2g, 102.1g/mol, 100mmol) are stirred at reflux in THF under exclusion of moisture for 3h. The product precipitates during the reaction. The reaction mixture is poured into methanol (1L), and left to stand overnight. The yellow precipitate is filtered off and purified by column chromatography in chloroform on silica. Yield: 3.73g (976.7g/mol, 3.81mmol, 76%).

1H-NMR (CDCl3, 400MHz): δ = 9.25-7.25 (m, 18H), 7.25-6.40 (m, 2H), 4.50-4.05 (m, 4H), 5.00-2.75 (m, 4H), 1.16 (t, 7Hz, 6H), 1.70-0.50 (m, 6H) ppm.
FD-HRMS (m/z): M+ Calcld for C34H28Br2O8 974.1090; found 974.1048.
Mp.: 271-273 °C
Tetraoctyl dipyreno[3,2-a:3',2'-h]anthracene-12,13,25,26-tetracarboxylate 12
Tetraoctyl 2,5-dibromo-1,4-phenylenebis((3-perylenyl)maleate) (0.40g, 1027.2g/mol, 0.32mmol), 12-aminotriicosane (0.33g, 339.6g/mol, 0.97mmol)\(^2\) and imidazole (10g) are stirred at reflux in \(\text{o-dichlorobenzene} (15g)\) under argon for 16h. After cooling to room temperature, the solidified mixture is dissolved in hot chloroform, the insoluble product is filtered off. The green diimide is purified by recrystallisation from boiling 1,2-dichlorobenzene and washing with hot chloroform and hot acetone on a glass frit. Yield: 0.366g (1410.4g/mol, 0.26mmol, 89%).

1^H-NMR (CDCl\(_3\), 400MHz): \(\delta = 10.98\) (s, 2H), 9.71 (s, 2H), 9.44 (d, 8Hz, 2H), 8.77 (d, 8Hz, 2H), 8.52 (d, 8Hz, 2H), 8.36 (d, 8Hz, 2H), 7.95 (t, 8Hz, 2H), 7.88 (t, 8Hz, 2H), 7.84 (t, 8Hz, 2H), 7.83 (d, 8Hz, 2H), 7.62 (t, 8Hz, 2H), 4.55 (m, 2H), 2.37 (m, 4H), 2.03 (m, 4H), 1.63-1.22 (m, 72H), 0.88 (t, 6Hz, 12H) ppm.

FD-HRMS (m/z): \(M^+\) Calcd for \(C_{16}H_{16}N_2O_4\) 1408.8935; found 1408.8967.

Mp.: >375°C.

References
$^1$H-NMR (CD$_3$SOCD$_3$, 400MHz)

$^{13}$C-NMR (CD$_3$SOCD$_3$, 100MHz)
$^1$H-NMR (CDCl$_3$, 400MHz)

$\text{C}_2\text{H}_5\text{O}_2\text{C}$

chloroform

water

ppm

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$^{13}$C-NMR (CDCl$_3$, 100MHz)

C$_2$H$_5$O$_2$C$\equiv$O

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$^1$H-NMR (CD$_3$SOCD$_3$, 400MHz)

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$^1$H-NMR (CDCl$_3$, 400MHz)

![NMR spectrum](image)

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$^{13}$C-NMR (CDCl$_3$, 100MHz)

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$^1$H-NMR (CD$_3$SOCD$_3$, 400MHz)

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$^{13}$C-NMR (CD$_3$SOCD$_3$, 100MHz)

O

DMSO
$^1$H-NMR (CDCl$_3$, 400MHz)

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$^1$H-NMR (CDCl$_3$, 400MHz)

[Chemical structure image]

chloroform

water

ppm

11.5 11 10.5 10 9.5 9 8.5 8 7.5 7 6.5 6 5.5 5 4.5 4 3.5 3 2.5 2 1.5 1 0.5 0 0 -0.5

ppm

8.5 8 7.5 7 6.5

ppm

4.2 3.7 3.2 2.7 2.2 1.7 1.2 0.7 0.2
$^1$H-NMR (CDCl$_3$, 400MHz)

![NMR spectra](image)

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H-NMR (CDCl$_3$, 400MHz)
$^{13}$C-NMR (CDCl$_3$, 100MHz)

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$^1$H-NMR (CDCl$_3$, 400MHz)
$^1$H-NMR (CD$_2$ClCDCl$_2$, 130°C, 400MHz)

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