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γ-(Hydroxyalkyl)naphthalene-tetracarboxdiimides: Organic White Pigments

Heinz Langhals*[a] and Ulrike Ritter[a]

Dedicated to Prof. Dr. H. Nöth on the occasion of his 80th birthday

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Naphthalene-1,8:4,5-tetracarboxdiimides were prepared from cyanoacetic acid and its alkylation, reduction and condensation with naphthalenetetracarboxylic dianhydride and exhibit strong light-scattering and opacifying properties. Applications are discussed.

Introduction

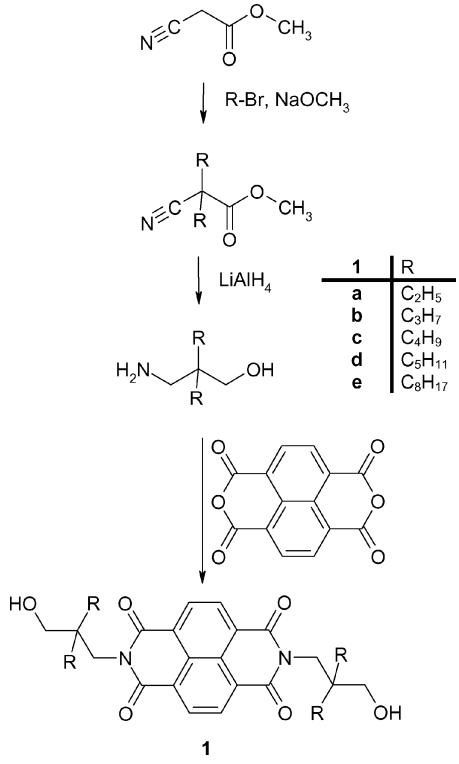
Inorganic colour pigments such as cinnabar, cadmium selenide or cadmium sulfide are being more and more replaced by organic pigments.[1] High colour strength and brilliance can be obtained with these materials and even more important is their low toxicity and easy biodegradability. On the other hand, organic white pigments have attained only little interest. Technical applications focus on titanium dioxide as the universal white pigment because of its chemical inertness with respect to acids, bases and solvents, its low toxicity and its high index of refraction (rutile, $n_D^{20} = 2.75$). Zinc oxide ($n_D^{20} = 2.03$) and zinc sulfide ($n_D^{20} = 2.37$) are used for more special applications; for example, lubricating effects are appreciated with respect to the latter and are caused by the arrangement in the crystal lattice. On the other hand, the easy reaction of the zinc-based pigments with acids limits their applications. Even the use of titanium dioxide may give rise to problems caused by photooxidation. This reaction is applied for self-cleaning surfaces being covered with a layer of TiO_2, however, the same reaction may cause undesired degradation effects in pigment applications because of the large surface of the particles with dimensions of a micron. Moreover, the chemical persistency of TiO_2 may cause long-lasting effects of such reactions. A biodegradable organic white pigment would bring about an appreciable progress, especially for mass products like paper. The white pigments of the wings of butterflies[2] are the purely organic-based pteridines and indicate the general possibility of the development of such organic white pigments. However, the synthesis of the pteridines as the natural white pigments still remains rather complicated[3] and prevents their broad technical application. The easy degradability[2d] is a further obstacle for their application. More easily accessible pigments would bring about an appreciable progress and was the subject of some investigations.[4]

Results and Discussion

A white pigment requires a high index of refraction because of the necessary light scattering. An intense absorption band in the UV close to the visible light range is suitable for such a realization because this would cause a pronounced anomalous dispersion in the UV and its extension into the visible being the normal dispersion would bring about a high index of refraction.

The naphthalene-1,8:4,5-tetracarboxdiimides fulfil these conditions for aliphatic substituents at the nitrogen atoms. The reported rose to red colour[5] of these compounds could be identified[6] to be caused by perylene-3,4:9,10-tetracarboxdiimides[7] formed as by-products of synthesis. However, synthesis under selected conditions and subsequent recrystallisation would result in pure colourless materials. Alkyl substituents with hydroxy groups in position 3 cause special dense packings in perylene dyes and protect the tetracarboxdiimide groups against hydrolysis.[8] Thus, we introduced such substituents into the naphthalene-tetracarboxdiimides starting with cyanoacetate according to Scheme 1, subsequent alkylation, reduction to the amino alcohol and condensation with naphthalene-1,8:4,5-tetracarboxylic dianhydride. Purely white powders were obtained after recrystallisation. The reflectivity of the solid **1d** is show in Figure 1 and indicates the strong light-scattering throughout the whole spectrum.

[a] Department of Chemistry and Biochemistry, LMU University of Munich,
Butenandtstr. 13, 81377 Munich, Germany
Fax: +49-89-2180-77700
E-mail: Langhals@lrz.uni-munchen.de



Scheme 1. Synthesis of **1**.

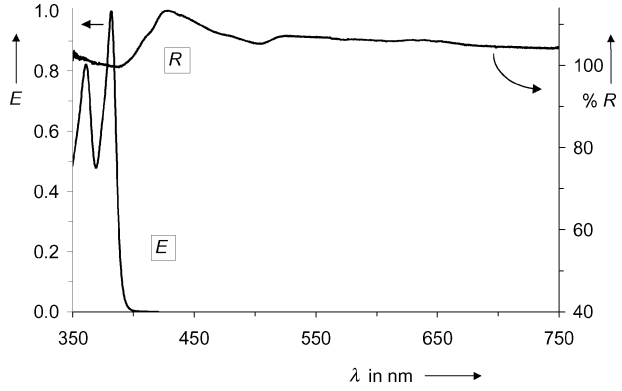


Figure 1. Reflectivity *R* of solid **1d** compared with the absorption spectrum in chloroform (*E*). The accuracy of measurements of reflectivity is limited by artefacts such as a weak solid-state fluorescence.

The absorption of **1d** in chloroform is shown for comparison and demonstrates the proximity of the absorption band to the visible. A high index of refraction is required for efficient light scattering (I_s) according to Equation (1) where *m* is the ratio of the indices of refraction of the pigment and the surrounding medium.

$$I_s \approx (m^2 - 1)^2/(m^2 + 2)^2 \quad (1)$$

An index of refraction of more than 1.6 is sufficient to get an impression of a white pigment in air because of an index of about unity for the latter. An even higher index of refraction is required in organic media such as dried linseed oil with an index of refraction of about 1.48. Thus, we dispersed the pigment **1d** for a test in a 71% solution of sucrose in distilled water with an index of refraction n_D^{20} = 1.472, and the material still remained a white, strongly opacifying pigment in spite of the high index of refraction of the medium.

Conclusions

Naphthalene-tetracarboxdiimides can be applied as white pigments both in air and in organic media and may replace inorganic white pigments for some application for opacifying. This is of special interest with respect to their use in bulk material production, for instance paper industry. The UV light protecting properties if **1** are of additional advantage.[9]

Experimental Section

General: IR spectra: Perkin–Elmer 1420 Ratio Recording Infrared Spektrometer, FT 1000. UV/Vis spectra: Varian Cary 5000 and Bruins Omega 20. NMR spectroscopy: Varian Vnmrs 300 (300 MHz), Vnmrs 600 (600 MHz). Mass spectrometry: Finnigan MAT 95.

Methyl 2-Cyano-2-octyldecanoate: Methyl cyanoacetate (18 mL, 200 mmol), 1-bromooctane (70 mL, 400 mmol; 2 equiv.) and 25% sodium methoxide solution in methanol (91 mL, 400 mmol, 2 equiv.) were allowed to react according to ref.[8]. Yield 43.53 g (67%) colourless liquid, b.p. 155–162 °C (9×10^{-3}–1.6×10^{-2} mbar). IR (ATR): $\tilde{\nu}$ = 2955 (s), 2925 (s), 2856 (s), 2244 (w), 1745 (s), 1458 (m), 1379 (w), 1232 (m), 1177 (w), 1137 (w), 1079 (w), 775 (w), 723 (w) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 7.0 Hz, 6 H, -CH_3) 1.30 (m, 22 H, -CH_2-), 1.55 (m, 2 H, -CH_2-), 1.76 (m, 2 H, -CH_2-), 1.88 (dt, ^3J = 4.0, ^2J = 13.3 Hz, 2 H, -CH_2-) 3.81 (s, 3 H, -OCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1, 22.6, 25.4, 29.1, 29.2, 31.8, 50.0, 53.2, 119.5, 169.9 ppm. MS (DEI$^+$/70 eV): *m*/*z* (%) = 324 (1), 323 (3) [M^+], 322 (3), 264 (15) [M^+ – CO_2CH_3], 212 (7), 211 (42) [M^+ – C_8H_{17}], 210 (6), 156 (9), 155 (100) [M^+ – C_8H_{17}, -CO_2CH_3], 154 (14), 39 (18). HRMS ($C_{20}H_{37}NO_2$): calcd. *m*/*z*: 323.2824, found *m*/*z*: 323.2836, Δ = 1.2 mmu. $C_{20}H_{37}NO_2$ (323.5) calcd. C 74.25, H 11.53, N 4.33; found C 74.29, H 11.41, N 4.30.

2-(Aminomethyl)-2-octyldecan-1-ol: Methyl 2-cyano-2-octyldecanoate (38.8 g, 120 mmol, 1 equiv.) and $LiAlH_4$ (5.92 g, 156 mmol, 1.3 equiv.) were allowed to react according to ref.[8] and purified by kugelrohr distillation in medium vacuum. Yield 24.5 g (68%) colourless liquid, b.p. 205–225 °C (1×10^{-3}–2×10^{-3} mbar). IR (ATR): $\tilde{\nu}$ = 3368 (w, br), 3300 (w, br), 1596 (w), 1466 (m), 1378 (w), 1051 (m), 721 (w) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 7.0 Hz, 6 H, -CH_3), 1.26 (m, 28 H, -CH_2-), 2.77 (s, 2 H, -CH_2-NH_2), 3.56 (s, 2 H, -CH_2-OH) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1, 22.7, 23.0, 29.3, 29.6, 30.6, 31.9, 50.1, 71.5 ppm. $C_{20}H_{45}NO$ (315.6): calcd. C 76.12, H 14.37, N 4.44; found C 76.42, H 13.93, N 4.51.

2,7-Bis[2-ethyl-2-(hydroxymethyl)butyl]benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (1a): Isochromeno[6,5,4-*def*]isochro-

mene-1,6,8-tetraone (410 mg, 1.53 mmol) and 2-(aminomethyl)-2-ethylbutan-1-ol[8] (600 mg, 4.60 mmol, 3 equiv.) in DMF (25 mL) were refluxed (bath 110 °C) for 2 h (colour change to red), cooled and further cooled with ice, quenched by the cautious addition of 2 N HCl (50 mL), collected by vacuum filtration, washed with a small amount of distilled water, dried in air at 110 °C, suspended in a small amount of methanol, refluxed with 10% K_2CO_3, collected by vacuum filtration, washed with a mixture of methanol/dist. water (1:1) and dried in air at 110 °C. Yield 202 mg (404 μmol, 26%) pale pink solid, m.p. 255–258 °C. IR (ATR): $\tilde{\nu}$ = 3550 (s), 3508 (m), 2967 (s), 2883 (m), 1702 (s), 1657 (s), 1580 (m), 1549 (w), 1454 (m), 1428 (w), 1372 (m), 1329 (s), 1247 (m), 1168 (w), 1105 (w), 1030 (w), 1001 (w), 889 (w), 772 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 0.94 (t, ^3J = 7.5 Hz, 12 H, -CH_3), 1.32 (qd, ^3J = 7.5, ^2J = 14.7 Hz, 4 H, -CH_2-), 1.41 (qd, ^3J = 7.5, ^2J = 14.9 Hz, 4 H, -CH_2-), 3.23 (d, ^3J = 7.6 Hz, 4 H, -CH_2-OH), 3.62 (t, ^3J = 7.6 Hz, 2 H, -CH_2-O*H*), 4.20 (s, 4 H, CH_2-NR_2), 8.79 (s, 4 H, CH_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 7.4, 23.7, 43.1, 43.7, 65.2, 126.5, 126.6, 131.6, 164.3 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 383 (26600), 362 (22000), 344 nm (13800 L mol^{-1} cm^{-1}). MS (ESI): *m*/*z* (%) = 641 (82) [M^+ + $^{35}Cl^-$], 605 (47) [M^+ – H^+].

2,7-Bis[2-(hydroxymethyl)-2-propylpentyl]benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (1b): Isochromeno[6,5,4-*def*]isochromene-1,3,6,8-tetraone (655 mg, 2.45 mmol), 2-(aminomethyl)-2-propylpentan-1-ol[8] (1.17 g, 7.34 mmol; 3 equiv.) and DMF (75 mL) were allowed to react analogously to **1a** and recrystallised two times from chloroform. Yield 750 mg (56%) pale pink, shiny solid, m.p. 199–201 °C. IR (ATR): $\tilde{\nu}$ = 3478 (s), 2953 (s), 2928 (m), 2871 (m), 1698 (s), 1642 (s), 1582 (m), 1458 (m), 1433 (m), 1374 (m), 1330 (s), 1244 (m), 1202 (m), 1161 (w), 1094 (m), 1039 (w), 1016 (m), 975 (w), 890 (w), 860 (w), 776 (m), 720 (w), 662 (w) cm^{-1}. ^1H NMR (300 MHz. $CDCl_3$): δ = 0.94 (t, ^3J = 7.3 Hz, 12 H, -CH_3), 1.34 (m, 12 H, -CH_2), 1.50 (m, 4 H, -CH_2), 3.20 (d, ^3J = 7.6 Hz, 4 H, -CH_2-OH), 3.70 (t, ^3J = 7.6 Hz, 2 H, -CH_2-O*H*), 4.20 (s, 4 H, -CH_2-NR_2), 8.79 (s, 4 H, CH_{ar}) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.96, 16.28, 34.38, 43.25, 43.99, 65.68, 126.5, 131.6, 164.3 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 383 (26600), 362 (22000), 344 nm (13400 L mol^{-1} cm^{-1}). MS (DEI$^+$, 70 eV): *m*/*z* (%) = 550 (15) [M^+], 520 (100) [M^+ – CH_3O], 422 (7), 410 (12), 409 (53), 294 (9), 281 (13), 268 (6). $C_{32}H_{42}N_2O_6$ (550.7): calcd. C 69.79, H 7.69, N 5.09; found C 69.42, H 7.69, N 4.96.

2,7-Bis[2-butyl-2-(hydroxymethyl)hexyl]benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (1c): Isochromeno[6,5,4-*def*]isochromene-1,3,6,8-tetraone (1.31 g, 4.89 mmol), 2-(aminomethyl)-2-butylhexan-1-ol[8] (2.75 g, 14.7 mmol) and DMF (70 mL) were allowed to react analogously to **1a**. Yield 985 mg (1.62 mmol, 33%) pale pink, shiny solid; a colourless solid was obtained after several recrystalliations from chloroform, m.p. 232–234 °C. IR (ATR): $\tilde{\nu}$ = 3480 (s), 2953 (s), 2930 (s), 2864 (m), 1698 (s), 1646 (s), 1581 (m), 1459 (m), 1432 (m), 1367 (m), 1330 (s), 1244 (s), 1199 (w), 1150 (w), 1099 (w), 1024 (m), 884 (w), 865 (w), 776 (w), 720 (w), 660 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 0.92 (t, ^3J = 7.1 Hz, 12 H, -CH_3), 1.22–1.33 (m, 20 H, -CH_2-), 1.38–1.46 (m, 4 H, -CH_2-), 3.21 (d, ^3J = 7.6 Hz, 4 H, -CH_2-OH), 3.67 (t, ^3J = 7.6 Hz, 2 H, -CH_2-O*H*), 4.21 (s, 4 H, -CH_2-NR_2), 8.79 (s, 4 H, CH_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 14.07, 23.60, 25.1, 31.65, 43.02, 43.98, 65.70, 126.51, 131.58, 164.25 ppm. MS (ESI): *m*/*z* (%) = 641 (82) [M^+ + $^{35}Cl^-$], 605 (47) [M^+ – H^+]. UV/Vis ($CHCl_3$): λ_{max} (ε) = 383 (26600), 362 (21900), 344 nm (13400 L mol^{-1} cm^{-1}). $C_{36}H_{50}N_2O_6$ (606.8): calcd. C 71.26, H 8.31, N 4.62; found C 71.11, H 8.37, N 4.62.

2,7-Bis[2-(hydroxymethyl)-2-pentylheptyl]benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (1d): Isochromeno[6,5,4-*def*]isochromene-1,3,6,8-tetraone (1.31 g, 4.89 mmol), 2-(aminomethyl)-2-pentylheptan-1-ol[8] (3.16 g, 14.7 mmol) and DMF (75 mL) were allowed to react analogously to **1a**. Yield 575 mg (867 μmol, 18%) pale pink, shiny solid and colourless solid after several recrystallisations from chloroform, m.p. 226–229 °C. IR (ATR): $\tilde{\nu}$ = 3486 (s), 2930 (s), 2862 (m), 1698 (s), 1644 (s), 1581 (m), 1460 (m), 1431 (w), 1413 (w), 1369 (w), 1330 (s), 1242 (m), 1209 (w), 1191 (w), 1150 (w), 1104 (w), 1058 (w), 1026 (m), 890 (w) 863 (vw), 778 (w) 719 (w) 662 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 0.92 (t, ^3J = 7.2 Hz, 12 H, -CH_3), 1.19–1.37 (m, 28 H, -CH_2-), 1.38–1.48 (m, 4 H, -CH_2-), 3.20 (d, ^3J = 7.6 Hz, 4 H, -CH_2-OH), 3.65 (t, ^3J = 7.6 Hz, 2 H, -CH_2-O*H*), 8.79 (s, 4 H, CH_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 14.12, 22.59, 31.95, 32.79, 43.10, 65.72, 126.50, 131.57, 164.24 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 383 (26600), 362 (22000), 344 nm (13800 L mol^{-1} cm^{-1}). MS (ESI): *m*/*z* (%) = 697 (68) [M^+ + $^{35}Cl^-$], 661 (42) [M^+ – H^+]. $C_{40}H_{58}N_2O_6$ (662.9): calcd. C 72.47, H 8.82, N 4.23; found C 72.41, H 8.72, N 4.16.

Bis[2-(hydroxymethyl)-2-octyldecyl]benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (1e): Isochromeno[6,5,4-*def*]isochromene-1,3,6,8-tetraone (1.50 g, 5.59 mmol), 2-(aminomethyl)-2-octyldecan-1-ol (5.30 g, 16.8 mmol) and DMF (170 mL) were allowed to react analogously to **1a**, and purified by column separation (silica gel 60, $CHCl_3$/H_3CCO_2H, 50:1). Yield 1.74 g (2.09 mmol, 37%) pale pink, shiny solid, m.p. 176–178 °C. R_f (silica gel, $CHCl_3$/H_3CCO_2H, 50:1): 0.5. IR (ATR): $\tilde{\nu}$ = 3481 (s), 2956 (m), 2921 (s), 2852 (s), 1699 (s), 1645 (s), 1580 (s), 1460 (s), 1432 (w), 1415 (w), 1387 (w), 1370 (w), 1331 (s), 1255 (w), 1245 (m), 1191 (w), 1152 (w), 1112 (w), 1094 (w), 1027 (w), 975 (w), 891 (w), 865 (w), 815 (w), 779 (w), 720 (w) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 7.0 Hz, 12 H, -CH_3), 1.20–1.33 (m, 50 H, -CH_2-), 1.36–1.45 (m, 4 H, -CH_2-), 1.54–1.60 (m, 2 H, -CH_2-), 3.20 (s, 4 H, -CH_2-NR_2), 3.66 (br. s, 2 H, -OH), 8.79 (s, 4 H, CH_{ar}) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.11, 22.66, 22.89, 29.31, 29.51, 29.53, 30.55, 30.57, 31.87, 31.95, 31.98, 43.08, 43.97, 65.69, 126.48, 131.56, 164.21, 164.23 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 383 (26900), 362 (22300), 344 nm (14000 L mol^{-1} cm^{-1}). MS (ESI): *m*/*z* (%) = 865.6 (100) [M^+ + $^{35}Cl^-$], 830.6 (44) [M^+ – H^+]. HRMS ($C_{52}H_{81}N_2O_5$): *m*/*z*: calcd. 831.6173, found 831.6290, Δ = 11.7 mmu. $C_{52}H_{82}N_2O_6$ (831.2): calcd. C 75.14, H 9.94, N 3.37; found C 75.15, H 10.18, N 3.36.

Acknowledgments

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