

Before each spectrum was measured, the film was submitted to an anodic galvanostatic step ($+38 \mu\text{A}/\text{cm}^2$), in order to attain the fully colored states. In these films the transmittance of the colored states is the same as the transmittance of the as-grown film. For $\lambda \geq 450 \text{ nm}$ (Fig. 4) there is a net dependence of the transmittance on the cathodic charge. The strongest transmittance change is located at 750 nm. The reported spectrally selective behavior of cobalt oxide films^[18] can be clearly seen in this figure.

The results described above clearly indicate the presence of the electrochromic effect in anodically grown cobalt oxide films. Work is in progress to improve the characterization of the system, and also to understand the complex electrochemical behavior of these materials.

Experimental

Adherent, homogeneous CoO_x films were anodically deposited on a transparent/conducting substrate (glass covered with SnO_2 , square resistivity $16 \Omega/\square$) with a current density of $76 \mu\text{A}/\text{cm}^2$; at this current density, no bubbles were observed during deposition. Deposition time was typically 20 minutes. The thickness of the film, as measured by profilometry was 145 nm. The electrolyte was a $10^{-2} \text{ M Co(NO}_3)_2 + 10^{-1} \text{ M CH}_3\text{COONa}$ solution, with pH 7.5; the counter electrode was a Pt sheet, conveniently located in the electrochemical cell. After deposition, the electrochemical/electrochromic properties of the films were analyzed in degassed 10^{-1} M KOH electrolyte, in a three electrode cell (Pt wire counter electrode, saturated calomel reference electrode) with optical windows. A PAR 173 potentiostat-galvanostat associated with a PAR 175 function generator was used in the electrochemical experiments. Data were recorded in a analogical X-Y (X-T) recorder. Monochromatic transmission (He-Ne laser, $\lambda = 632.8 \text{ nm}$) was recorded in situ, by means of a versatile optical bench; spectral transmittance in the visible-near infrared were measured in a Lambda-9 double beam spectrophotometer (Perkin-Elmer Corp.), by placing the electrolytic cell in the optical path of one of the beams, at different color states. In this work, all transmittance values are quoted relative to the system cell + electrolyte, to which the 100% value is attributed.

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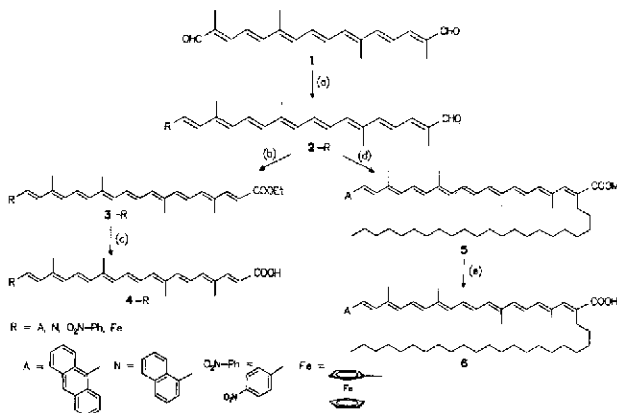
Properties of Amphiphilic Terminally Substituted Conjugated Nonaene- and 2-Docosylnonaene Carboxylic Acids in Monolayers at the Air-Water Interface**

By Franz Effenberger,* Paul Meller, Helmut Ringsdorf,* and Hubert Schlosser

Dedicated to Professor Michael Hanack on the occasion of his 60th birthday

In recent years, the development of compounds which may be employed in the storage and transfer of information on a molecular level has gained increasing importance.^[1, 2] Apart from the synthetic challenge, the formation of ordered supramolecular structures from these compounds merits investigation.^[1, 3] In the present communication, we report the synthesis of conjugated nonaene- and 2-docosylnonaene carboxylic acids with different terminal substituents. These substituents have been chosen so that their spectroscopic properties differ from those of the polyene chain; they also have specific electron donor, electron acceptor or redox properties to allow for specific and selective excitation (energy intake). Because of the amphiphilic character of these compounds, pressure-area isotherms were determined in monolayers at the air-water interface. Their microscopic structure was observed in situ by fluorescence microscopy.

The nonaene carboxylic acids **4-R**, with end groups R = 9-anthryl (A), 1-naphthyl (N), *p*-nitrophenyl ($\text{O}_2\text{N-Ph}$) and ferrocenyl (Fe), as well as the 9-anthryl-substituted 2-docosylnonaene carboxylic acid **6**^[4] were synthesized from crocetin dialdehyde **1**^[5] by Wittig- and Wittig-Horner olefinations.^[2, 6] Intermediates of this synthetic route were the octaene aldehydes **2-R**, and the esters **3-R** and **5** (Scheme 1).



Scheme 1. The synthetic routes; for explanations see *Experimental*.

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The resulting polyenes were obtained as *E/Z* mixtures after column chromatography. The dominant all-*E* component could be further enriched by crystallization (Scheme 1). The isomers were discernible by UV/vis and ¹H-NMR spectroscopy.^[2a, 6]

Table 1. UV/vis-absorption data [λ /nm (log ϵ)] of polyenes 2–6 [a], [b].

R	2-R	3-R	4-R	5	6
A	478 (4,93) 254 (4,91)	480 (4,92) 255 (4,84)	481 (5,01) 254 (4,94)	474 (4,92) 254 (4,84)	475 (4,92) 254 (4,86)
N	498 (4,81) (s) 476 (4,78)	508 (4,89) (s) 481 (4,97) 458 (4,78) (s)	510 (5,01) (s) 485 (5,06)		
	228 (4,33)	228 (4,37)	228 (4,46)		
O ₂ N-Ph	515 (4,99) (s) 491 (5,03)	524 (4,99) (s) 498 (5,04)	527 (s) 500		
Fe		504 (4,81) (s)	509 (4,86) (s)		
	474 (4,88)	477 (4,89)	481 (4,93)		

[a] In CH₂Cl₂. [b] Concentration = 0.8 · 10⁻⁵ – 2 · 10⁻⁵ M. (s) = Shoulder.

The UV/vis absorption spectra of the polyenes 2–6 (Table 1, Fig. 1) are similar to those reported for diarylpolyenes and carotenoids.^[7] The 9-anthryl- and 1-naphthyl-substituted compounds 2-A, 3-A, 4-A, 5, 6 and 2-N, 3-N, 4-N display absorption maxima around 255 nm or 228 nm,^[2a] corresponding to excitation of the ¹B_v-states of either anthracene or naphthalene.^[8]

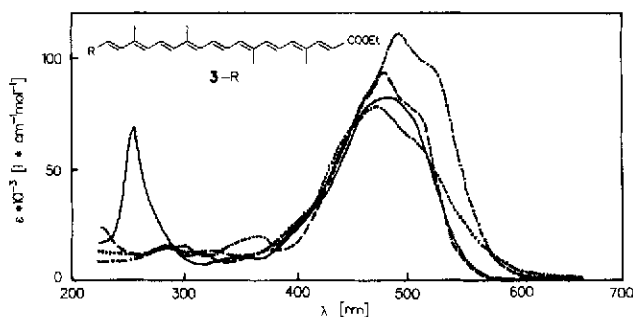


Fig. 1. UV/vis absorption spectra of different substituted 3-R in CH₂Cl₂ at 25°C; R = A (—) (*c* = 2.0 · 10⁻⁵ M), R = N (---) (*c* = 2.0 · 10⁻⁵ M), R = O₂N-Ph (-·-) (*c* = 1.0 · 10⁻⁵ M), R = Fe (···) (*c* = 1.01 · 10⁻⁵ M).

This localized excitation of the terminal anthryl and naphthyl groups is due to the plane of the aryl end groups being twisted severely with respect to the σ -bond plane of the polyene system. This twist arises from steric interaction between the aryl hydrogen atoms in the *peri*-position and the hydrogen atoms of the first C–C double bond of the polyene chain.^[2b, 9] For the *p*-nitrophenyl polyenes, in contrast, the arene π -system in fact participates in the overall conjuga-

tion; consequently, the intense longest-wavelength absorption of compounds 2-O₂N-Ph, 3-O₂N-Ph, 4-O₂N-Ph experiences a 15–19 nm bathochromic shift.

Amphiphilic behavior, i.e. the possibility to form ordered structures in monolayers, was expected for the nonaene acids 4-R and 6.^[10] The behavior of the polyenic acids 4-R in monolayers is summarized in Figure 2.^[11] Despite the rigid polyene chain, typical monolayer behavior is observed, giving pressure–area isotherms in the temperature range 5–40°C. All four nonaene carboxylic acids show similar isotherms, the formation of well-defined solid-analogous phases^[10] being a direct consequence of the rigidity of the hydrophobic polyene chain.

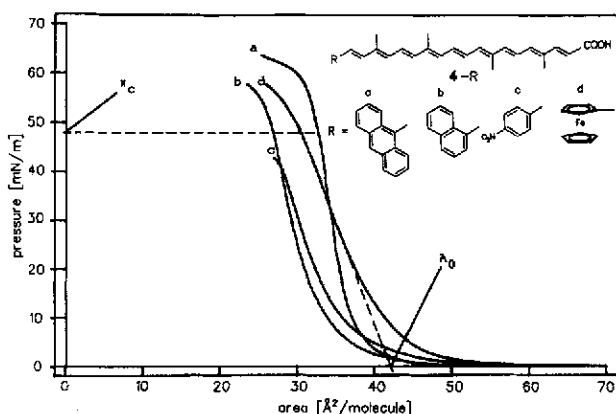


Fig. 2. Pressure–area diagrams of different substituted nonaene carboxylic acids 4-R at 20°C, subphase H₂O (Millipore); A₀: extrapolated molecular area of 4-Fe at zero pressure, π_c : collapse pressure.

The molecular area of the polyenic acid chain may be determined as the point of intersection of a tangent to the pressure–area isotherms.^[13] Figure 2 shows values from 33 to 42 Å²/molecule depending on the size of the end groups (Table 2).

Due to the regular methyl branching, the molecular area is of course higher than that of a straight alkyl chain (20 Å²/molecule).^[10] It is in good agreement, on the other hand, with the 28 Å²/molecule, determined for the structurally related β -*apo*-8'-carotenoidic acid^[14] with a cyclohexenyl end

Table 2. Collapse pressures π_c [mN/m] and extrapolated area at zero pressure A₀ (Å²/molecule) of nonaene acids 4-R and 6.

	4-A	4-N	4-O ₂ N-Ph	4-Fe	6
π_c	53[a] 52[b] 54[c]	51[a]	39[a]	48[a]	21[b] 43[c]
A ₀	38[a] 48[b] 44[c]	33[a]	36[a]	42[a]	64[b] 63[c]

[a] Subphase: H₂O. [b] Subphase: H₂O/pH 9/NaOH. [c] Subphase: H₂O/pH 9/NaOH/0.5 mM BaCl₂.

group. These results indicate an orthogonal orientation of the polyene molecules relative to the water surface.

Figure 3 shows the spreading behavior of 9-anthrylnonaene acid 4-A on different subphases. The molecular area increases from 38 to 48 Å²/molecule upon going from a neutral to an alkaline subphase (H₂O/pH 9/NaOH). This is due to the formation of charged carboxylate head groups since electrostatic repulsion enhances the intermolecular distance. Upon addition of barium ions to the alkaline sub-

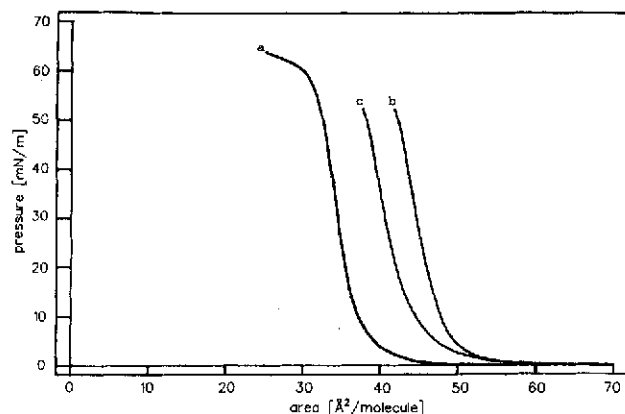


Fig. 3. Pressure area diagrams of 9-anthrylnonaene acid 4-A at 20°C; a) subphase H₂O b) subphase H₂O/pH 9/NaOH c) subphase H₂O/pH 9/NaOH/0.5 mM BaCl₂.

phase (H₂O/pH 9/ NaOH/0.5 mM BaCl₂), the molecular area decreases to 44 Å²/molecule. Barium carboxylate ion pairs are formed on the water surface, and since two chains are bonded per Ba²⁺ ion, a more compact packing of the hydrophobic chains becomes feasible.

9-Anthryl-2-docosylnonaene acid 6 presents an excellent illustration of how varying the constitution of the subphase affects monolayer formation (Fig. 4).

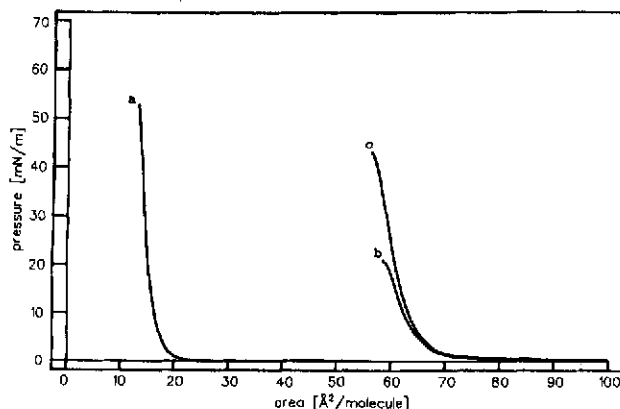


Fig. 4. Pressure-area diagrams of 9-anthryl-2-docosylnonaene acid 6 at 20°C; a) subphase H₂O b) subphase H₂O/pH 9/NaOH c) subphase H₂O/pH 9/NaOH/0.5 mM BaCl₂.

It is important to note that the average molecular area at collapse pressure, measured at 20°C on a pure water subphase, is below that for a two-dimensional ordered monolayer assuming a compact chain packing. A molecular area of 17 Å²/molecule is derived from the curve in Figure 4a which is far less than the theoretical value for a dual-chain amphiphilic molecule, calculated by addition of the molecular areas of 4-A (38 Å²/molecule) and of a saturated alkyl chain (20 Å²/molecule).^{11,10} This discrepancy is a clear indication that the polyenic acid 6 does not form well-defined monolayers on water (pH 5.8–6.0). An ordered monolayer is obtained only using alkaline subphases (H₂O/pH 9/ NaOH), with the expected molecular area of 64 Å²/molecule. The significantly lower collapse pressure (21 mN/m, see Table 2) indicates the monolayer to be decidedly less stable on an alkaline medium. Upon addition of BaCl₂ (H₂O/pH 9/NaOH/0.5 mM BaCl₂), however, the collapse pressure is more than doubled (43 mN/m), i.e. the stability of the monolayer appears dramatically enhanced. The rigidity of the monolayer of compound 6 does not appear reduced by the mobile docosyl side chain, as compared with that of the polyenic acids 4-R.

Figure 5 presents the microscopic structure of a monolayer of 4-A mixed with 1–2 mol-% of a fluorescent lipid analogon 1-palmitoyl-2-[N-7-nitro-2,1,3-benzo-oxadiol-4-yl-amino-caproyl]phosphatidyl-choline (NBD-PC).

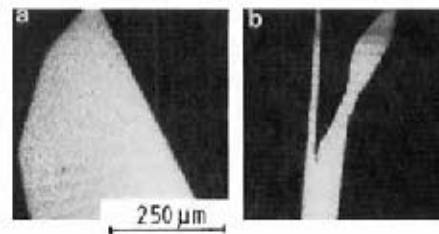


Fig. 5. Epifluorescence microscopy of anthracene polyene carboxylic acid 4-A at 20°C and surface pressure of 1–5 mN/m on alkaline subphase (pH 9). Concentration of fluorescence dyestuff NBD-PC was 1 mol-%. a) Clearly visible are the clean edges of a polyenic-acid monolayer which is very homogeneous within regions of polyenes and shows almost no dyestuff molecules. b) At higher surface pressures only small fluorescent channels are visible.

At low pressures (≥ 1 mN/m), most of the dyestuff is displaced from the solid-analogous phase of the polyenic acid monolayer. The emitted fluorescence intensity becomes visible only in small channels where the dyestuff particles are concentrated between homogeneous monolayer regions (Fig. 5b). For all compounds studied, these monolayer regions appear homogeneous upon microscopic observation; their rigidity renders them highly stable on aqueous subphases (>48 h). This rigidity so far also prevented the transfer of monolayers onto solid supports, and the formation of Langmuir-Blodgett films without cleaving the lateral structure. Even if increasing molar fractions of saturated lipid analogues were added to the spreading solution, no satisfactory transfer conditions were obtained. Any future synthetic

approach will therefore have to include additional mobile elements built into the polyenic acid, which take the viscoelastic conditions during the transfer into account.^[15]

Experimental

(a) 2-R: analogous to [2a, 6]. (b) 3-R: 2-R, $\text{Ph}_3\text{P}=\text{CHCOOEt}$ (1:6)/ $\text{CH}_2\text{Cl}_2/40^\circ\text{C}$; various reaction times; chromatography on $\text{SiO}_2/\text{CH}_2\text{Cl}_2$; recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$. 3-A: 73 h; 45%; 95% all-*E* (HPLC); m.p. 183–184°C. 3-N: 68 h; 56%; 100% all-*E* (HPLC); m.p. 200–201°C. 3-O₂N-Ph: 60 h; 52%; 98% all-*E* (HPLC); m.p. 211–212°C. 3-Fe: 52 h; 43%; 100% all-*E* (¹H-NMR); m.p. 172–173°C. (c) 4-R: 3-R, 2 N ethanolic KOH/ $\text{CH}_2\text{Cl}_2/\text{EtOH}$ (1:1)/18 h/55°C; acidifying with ca. 1 N HCl; extraction with CH_2Cl_2 ; washing with water; chromatography on $\text{SiO}_2/\text{CH}_2\text{Cl}_2/\text{EtOH}$ (100:1 or 100:5). 4-A: 73 h; m.p. 197–198°C. 4-N: 80%; m.p. 210–211°C. 4-O₂N-Ph: 82%; m.p. 229–231°C. 4-Fe: 63%; m.p. 228–230°C. (d) 5: 2-A, 1 N methanolic NaOCH₃, $\text{CH}_3(\text{CH}_2)_{21}\text{CHPO}(\text{OEt})_2\text{CO}_2\text{CH}_3$ (1:23.5:5)/ $\text{CH}_2\text{Cl}_2/90\text{ h}/40^\circ\text{C}$; aqueous work up; chromatography on $\text{SiO}_2/\text{CH}_2\text{Cl}_2$; recrystallization from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$; 36%; 72% all-*E* (HPLC); m.p. 106°C. [$\text{CH}_3(\text{CH}_2)_{21}\text{CHPO}(\text{OEt})_2\text{CO}_2\text{CH}_3$: from $\text{CH}_3(\text{CH}_2)_{21}\text{CHBrCO}_2\text{CH}_3$, and $\text{P}(\text{OEt})_3$ analogous to [16]; 78%; b.p. 216–219°C/0.001 torr. $\text{CH}_3(\text{CH}_2)_{21}\text{CHBrCO}_2\text{CH}_3$: from $\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$ [17], SOCl_2 , Br_2 , CH_3OH analogous to [18]; recrystallization (2×) from acetone; 44%; m.p. 49–52°C]. (e) 6: analogous to 4-A (c); 42 h/70°C; CH_2Cl_2 phase: washing with NaCl solution; chromatography on $\text{SiO}_2/\text{CH}_2\text{Cl}_2/\text{EtOH}$ (95:5); 42%; m.p. 139–140°C.

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Pillared Randomly Interstratified Clay as a Highly Heat-Stable Catalytic Solid**

By Kazuo Urabe*, Naoki Kouno, Hiroaki Sakurai, and Yusuke Izumi

Pillared clay is one of the most fascinating advanced catalysts^[1] because it has uniformly distributed active sites in the bulk, and molecular-sieve microporosity like the zeolites. The number of pillared variants has been increased further with the use of positively charged sol particles^[2] as pillaring agents or layered host compounds other than clay.^[3] However, the central problem^[1b,4] to be overcome is the lower thermal stability of pillared clay compared to that of zeolites. A solution to this problem was recently provided by Chinese work^[5] on the application of rectorite as the host clay for the ever-popular 'Al₁₃' Keggin-ion pillars.^[1b,6] This material belongs to the class of regularly interstratified clays and leads to a heat-stable microporous solid. Unfortunately, rectorite is inconvenient as a starting material because it occurs rarely in nature. Here, we report for the first time, a pillared, randomly interstratified clay which not only exhibits a higher thermal stability and catalytic efficiency than that of pillared rectorite (PR) but is also easily prepared from a synthetic clay available as synthetic mica-montmorillonite (SMM).^[6,7]

Figure 1 shows the X-ray diffraction patterns of various pillared clays. For comparison purposes, a montmorillonite was employed as non-interstratified but typical smectite clay. Pillared montmorillonite (PM) calcined at 673 K for 4 h shows basal reflection peaks with basal spacing, d_{001} , of 17.4 Å, indicating the pillared structure with an interlayer spacing of 7.8 Å. Calcining this material at high temperature (1073 K) brings about the almost total disappearance of the

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