Donor–Acceptor Oligoenes with a Locked all-*trans* Conformation: Synthesis and Linear and Nonlinear Optical Properties

Ulf Lawrentz,*[a] Walter Grahn,†[a] Katarzyna Lukaszuk,[b] Christopher Klein,[b] Rüdiger Wortmann,*[b] Andreas Feldner,[c] and Dieter Scherer*[c]

This work is dedicated to Prof. Dr. Wolfgang Lüttke

Abstract: A general synthetic approach to variously polarised merocyanines and a cyanine with enhanced thermal and (photo)chemical stability by a locked all-*trans* conformation (derived from a rigidified hexatriene unit and a variety of common donor and acceptor groups) is presented as well as a systematic study of their (non)linear optical properties. Apart from the UV/Vis absorption and fluorescence behaviour, the ground- and excited-state dipoles, the first-, second- and third-order molecular polarisabilities were determined by electro-optical absorption measurements (EOAM) and degenerate four-wave mixing (DFWM) techniques in solution. Large values for the second- and third-order polarisability up to $\beta_0 = 461 \times 10^{-50}\,\mathrm{C\,V^{-2}\,m^3}$ (1242×10^{-30} esu) and $|\gamma_{LL}| = 183 \times 10^{-60}\,\mathrm{C\,V^{-3}\,m^4}$ (15×10^{-34} esu) were found. The linear and nonlinear optical properties were related to the ground-state polarisation and the resonance structure of the chromophores. In order to reveal the influence of the length of the polymethinic chain (number of π electrons within the chromophore), some lower homologues shortened by one C=C (double) bond were also taken into account. The unexpectedly high γ values of some of the merocyanines cannot be explained by a two-level model. Molecular vibrational third-order polarisabilities (calculated from absolute Raman intensities in solution) were qualitatively correlated to the DFWM results. Furthermore, the dependence of the ^{13}C NMR chemical shifts of the polymethinic carbons within the merocyanines upon ground-state polarisation was investigated and compared to those within a corresponding cyanine.

Keywords: donor–acceptor systems · fluorescence · NMR spectroscopy · nonlinear optics · polymethines

Introduction

The synthesis of organic molecules with good nonlinear optical (NLO) properties is of current interest with respect to a fundamental understanding of the structure–property relationships on the one hand and a potential application in the field of optical data processing and storage on the other. The response of any NLO-active molecule induced by a perturbing electric field (E), which can be the propagating electromagnetic wave of a laser beam, is ususally defined by Equation (1), in which α is the molecular first-order (linear) polarisability, β the second- and γ the third-order molecular polarisability.[1]

$$P = \alpha \cdot E + 1/2!(\beta : EE) + 1/3!(\gamma \vdots EEE) + \ldots \quad (1)$$

Donor–acceptor systems in general have been investigated extensively in this field and were used to establish much of the basic information about optical nonlinearity in organic matter. The merocyanines **A**–**C** are such "push–pull" molecules bearing both an electron-donating (Do) and withdrawing endgroup (A) linked by an oligoene as a π-conjugated system.

Their optical properties determined by the electronic wavefunctions of the ground and first-excited state (two-level model) depend strongly on the relative electron-donating and

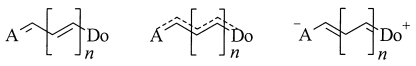
[a] Prof. Dr. W. Grahn,† Dipl.-Chem. U. Lawrentz
Institut für Organische Chemie
Technische Universität Braunschweig
Hagenring 30, 38106 Braunschweig (Germany)
E-mail: u.lawrentz@tu-bs.de

[b] Prof. Dr. R. Wortmann, Dr. K. Lukaszuk, Dipl.-Chem. C. Klein
Institut für Physikalische Chemie
Universität Kaiserslautern
FB Chemie, Erwin-Schrödinger-Strasse 52/528
67633 Kaiserslautern (Germany)
Fax: (+49) 631-2052750
E-mail: rwortman@rhrk.uni-kl.de

[c] Dipl.-Phys. D. Scherer, Dr. A. Feldner
Lehrstuhl für Experimentalphysik II, Universität Bayreuth
Universitätsstrasse 30, 95440 Bayreuth (Germany)
Fax: (+49) 921-552621
E-mail: dieter.scherer@uni-bayreuth.de

[†] Deceased August 15, 2001

  0947-6539/02/0807-1573 $ 20.00+.50/0



A **B** **C**

withdrawing strengths of the endgroups, on the length of the π system and on the solvent polarity and can be roughly approximated by mixing a neutral (**A**) and a charge-separated resonance form (**C**). Increasing contribution of the latter leads to more polarised molecules, and the influence of this polarisation on the (non)linear order polarisabilities was investigated experimentally[2] and by various computational methods.[3, 4] Hence molecules with maximised polarisabilities for specific applications can be achieved by tuning their polarisation, and their suitability can be expressed by different figures-of-merit (FOMs), as will be outlined below.[5]

Though simple oligoenes with their excellent electronic transmission properties, which allow charge separation even over long intramolecular distances,[6] seem to be superior to other conjugated systems such as oligo-(hetero)aromatics for use as π bridges in new, more efficient NLO chromophores, their conformational flexibility (twisting and *cis/trans*-isomerisation) affects the optimal conjugation and, in addition, their low thermal and (photo)chemical stabilities prevent them from device fabrication. Sufficient stability and a defined molecular structure in conformationally locked oligoenes can be attained by incorporating two or more conjugated C=C (double) bonds into an alicyclic ring system. This does not affect their optical transmittance, and some examples were reported more than 25 years ago.[7, 8] Much work following this principle was published within the last few years, covering merocyanines with one,[9] two[10, 11] and three[11, 12] rigidified C=C (double) bonds and aromatic donor groups. Derivatives with the (nitrogen) donor atom tethered directly to the oligoenic unit have also been reported.[13–15]

According to the model of mixing the resonance structures mentioned above, merocyanines can be classified qualitatively into three subgroups: Neutral *polyene-like* merocyanines containing endgroups with a weak to moderate electronic character are mainly described by **A** in their electronic ground state and exhibit an intramolecular charge transfer (ICT) upon optical excitation. This leads to a large change in the molecular geometry (and therefore very broad absorption bands in the UV/Vis spectra) and an increase in dipole moment. Maximised positive β values can be obtained as well as moderate to high positive values for γ. The use of endgroups with stronger donor or acceptor properties leads to merocyanines of the cyanine type (*neutrocyanines* **B**) with both limiting forms contributing 50% to the ground and excited state of the molecules (cyanine limit). Instead of the ICT, a charge resonance (CR) within the polymethinic chain occurs, with little or even no change in dipole moment and geometry.[16] For this reason very sharp and intense absorption bands in the UV/Vis spectrum are observed. Furthermore they are expected to show maximised negative γ values, but vanishing β ones. Charge-separated *betaines* such as **C** exhibit high ground-state dipole moments that are reduced by a back transfer of charge upon optical excitation. In nearly betaine-like compounds, maximised negative β and moderate to high positive γ values can be obtained.

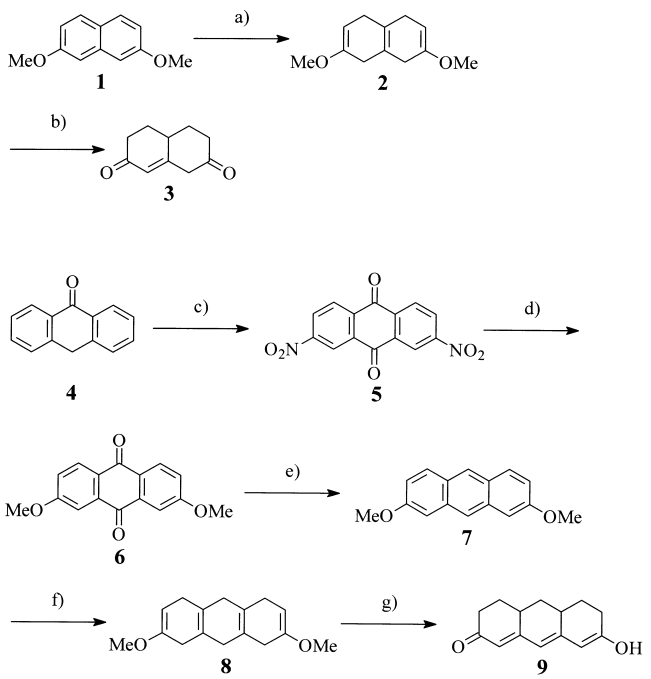
Since all shades of polarisation between these three limiting cases occur, different parameters for a quantitative description have been introduced, for example, the degree of bond length alternation (BLA) within the methine chain[3] (accessible by X-ray crystallography) and the c^2 resonance parameter[17] (determined by UV/Vis spectroscopy and electro-optical absorption measurements (EOAM) in solution), which is similar to the parameter MIX introduced by Blanchard-Desce et al.[18] The experimental values for the BLA (defined as the difference between the average lengths of adjacent C=C and C–C bonds of the polymethinic unit) and the c^2 parameter [defined below in Eq. (2)] range from BLA = –10 pm and $c^2 = 0$ for undisturbed oligoenes (**A**) to BLA = +10 pm and $c^2 = 1.0$ in fully charge-separated betaines (**C**). Perfect bond length equalisation (BLA = 0 pm and $c^2 = 0.5$) is observed in symmetric cyanines (**B**).

Abstract in German: *Die tragfähige Synthese einer Reihe unterschiedlich stark polarisierter, thermisch und photochemisch stabilisierter Merocyanine und eines Cyanins mit einer sterisch fixierten all-trans-Hexatrien-Untereinheit wird vorgestellt. Die systematische Untersuchung der (nicht)linear-optischen Eigenschaften dieser Verbindungen umfasst neben Absorptions- und Fluoreszenzspektroskopie im UV/VIS-Bereich die Bestimmung der Dipole im Grund- und Anregungszustand und der Polarisierbarkeiten erster bis dritter Ordnung mittels elektrooptischer Absorptionsmessungen (EOAM) sowie entarteter Vier-Wellen-Mischung (DFWM) in Lösung. Gefunden wurden z. T. sehr hohe Werte für die Polarisierbarkeiten zweiter und dritter Ordnung von* $\beta_0 = 461 \times 10^{-50}\ C V^{-2} m^3$; $(1242 \times 10^{-30}$ *esu) und* $|\gamma| = 183 \times 10^{-60}\ C V^{-3} m^4$; $(15 \times 10^{-34}$ *esu). Die gemessenen (nicht)linear optischen Eigenschaften werden anhand der Polarisation des Grundzustandes der Verbindungen diskutiert. Der Einfluss der Methinkettenlänge (d. h. der Anzahl der π-Elektronen innerhalb des Chromophors) wird durch Vergleich mit einigen um eine C=C-(Doppel)bindung verkürzten homologen Chromophoren untersucht. Die unerwartet hohen γ-Werte einiger Merocyanine lassen sich nicht anhand eines Zwei-Niveau-Modells erklären. Vibronische Polarisierbarkeiten dritter Ordnung, die aus Raman-Messungen in Lösung erhalten wurden, können jedoch qualitativ mit den DFWM-Ergebnissen korreliert werden. Die* ^{13}C *NMR chemischen Verschiebungen der methinischen Kohlenstoffatome innerhalb der Merocyanine werden mit denen eines entsprechenden Cyanins verglichen und auf eine Abhängigkeit von der Polarisation des Grundzustandes untersucht.*

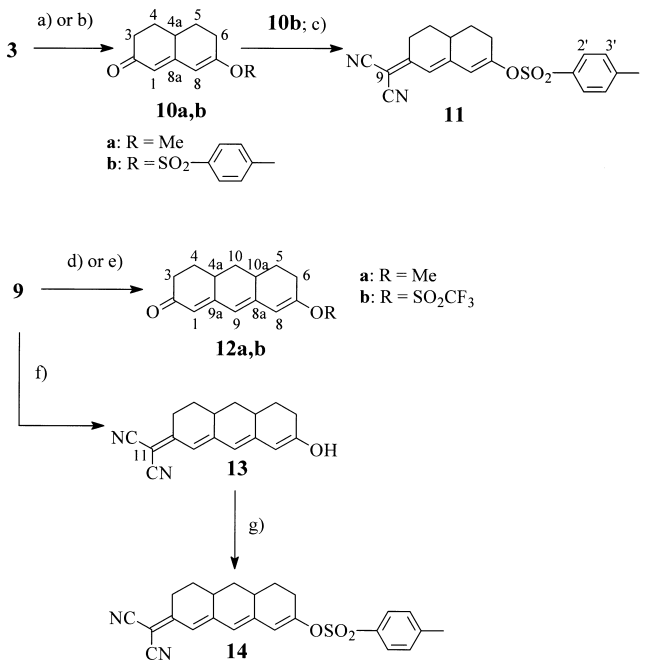
Results

Synthesis: The precursors for the conformationally fixed pentadiene and hexatriene units were prepared as outlined in Scheme 1.

  0947-6539/02/0807-1574 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 7



Scheme 1. Synthesis of the rigidified precursors **3** and **9**: a) Li, NH_3, diethyl ether, EtOH, −40 °C; b) 10% HCl, ethyl acetate, EtOH, reflux; c) 1. 100% HNO_3, 5 °C, 2. HOAc, reflux; d) MeOH, NaOH, reflux; e) Zn, 2N NaOH, toluene, reflux; f) 1. Li, NH_3, THF, −40 °C, 2. EtOH, Li, −60 °C; g) 1N HCl, 80 °C.



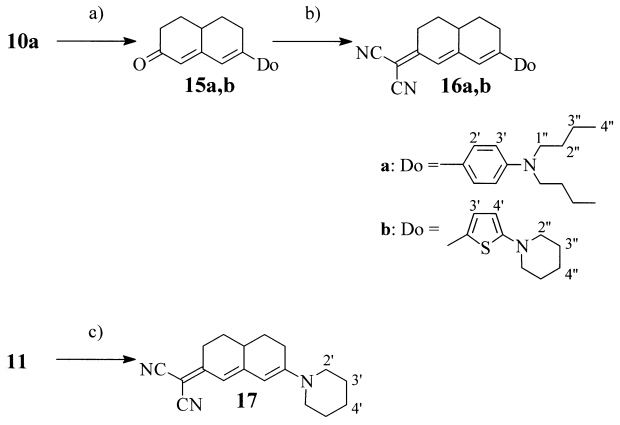
Scheme 2. Synthesis of the precursors **11**, **12**, and **14**: a) MeOH, toluene, *p*-TosOH, reflux; b) *p*-TosCl, Et_3N, THF, 25 °C; c) malonitrile, piperidine, HOAc, DMF, 25 °C; d) MeOH, HCl conc, reflux; e) 1. NaH, DME, 25 °C, 2. $PhN(SO_2CF_3)_2$, −60 °C; f) malonitrile, piperidine, HOAc, DMF, 25 °C; g) *p*-TosCl, pyridine, $CHCl_3$, 0 °C.

The synthesis of the dione **3** from the commercially available 2,7-dimethoxynaphthalene (**1**) could be reproduced from the literature,[19] but a combination of known procedures was necessary to establish a five-step synthesis for the vinylogous acid **9** (a modification of the route described by Heilig and Lüttke).[8] Due to the simplicitiy of the reactions used, **9** is accessible on a scale of several tens of grams in an overall yield of 14%. Nitration of the commercially available anthrone (**4**) and subsequent oxidation resulted in 2,7-dinitroanthraquinone (**5**) (49%),[20] substitution of the nitro groups yielded **6** (57%),[21] which was reduced to give 2,7-dimethoxyanthracene (**7**) by a modified Clemmensen method (70%).[22] Birch reduction afforded the hexahydroderivative **8** (74%),[8] which was converted to the vinylogous carbocylic acid **9** (95%) under acidic conditions.[8]

These precursors could be furnished with different leaving groups (Scheme 2) to facilitate introduction of the appropriate donor groups.

The methyl ester **10a** was obtained in 83% yield by a method[23] that is superior to the original work.[19] The tosylate **10b** was accessible in 38% yield according to Carotti et al.[24] Introduction of the dicyanomethylidene acceptor to **10b** by the Knoevenagel reaction gave **11** in only about 25% yield.[25] The esterification of the vinylogous acid **9** with methanol to **12** could be reproduced from the literature,[8] and the triflate **12b** was prepared in 60% yield by using the mild triflating reagent *N*-phenylbistrifluoromethanesulfonimide by known methods.[26] Condensation of **9** with malonitrile afforded **13** in approximately 54% yield[25] as crude product with sufficient purity for subsequent reaction to the tosylate **14** (ca. 38%).[27]

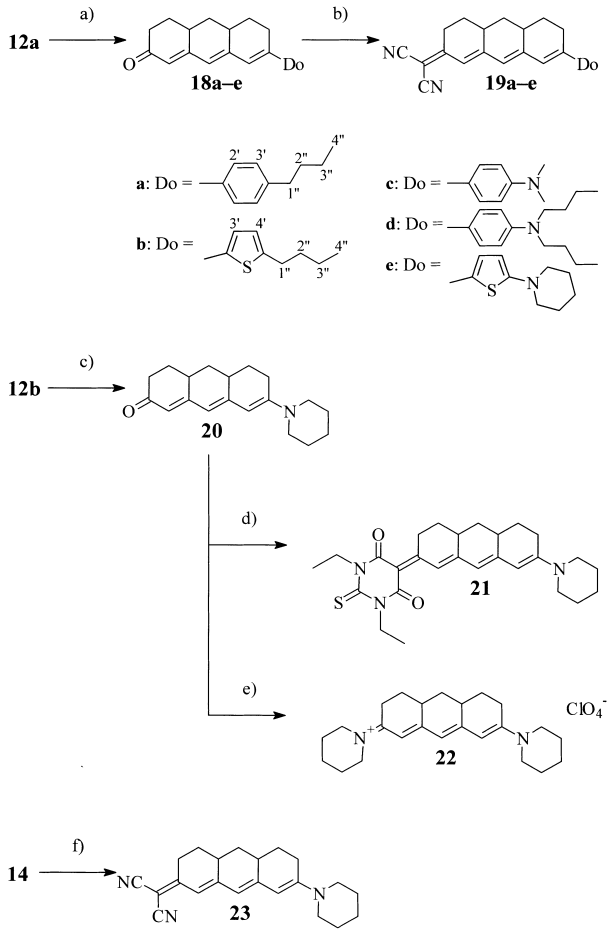
The synthesis of the merocyanines with two rigidified C=C (double) bonds, which will be named the "pentamethine series" in the following, from their above-mentioned precursors is shown in Scheme 3.



Scheme 3. Synthesis of the merocyanines **15**–**17**: a) LiAr, diethyl ether, −80 °C; b) 1. $Me_3O^+BF_4^-$, CH_2Cl_2, 0 °C, 2. malonitrile, pyridine, 80 °C; c) piperidine, NaH, MeCN, 70 °C.

The ketones **15a**,**b** with aromatic donor groups were prepared by treatment of the methyl ester **10a** with the corresponding lithiated dialkylaminoarenes followed by hydrolysis (16 and 37% yield, respectively; for similar procedures see refs. [11, 28]). Further reaction of **15a**,**b** by the Knoevenagel reaction with the method described by Meerwein et al.[29] afforded **16a**,**b** in 35 and 38% yield, respectively. Introduction of the piperidino donor directly to the oligoenic chain was achieved smoothly by substitution of the tosylate

group in **11** by the use of piperidine in the presence of sodium hydride in acetonitrile (ca. 74 % yield) for the formation of **17**; an analogous procedure gave the higher homologue **23** in approximately 41 % yield from **14** (Scheme 4).



Scheme 4. Synthesis of the merocyanines **18**–**21**, **23**, and the cyanine **22**: a) LiAr, THF, −80 °C; b) malonitrile, HOAc, (Ac_2O), piperidine, DMF, 80 °C; c) piperidine, NaH, MeCN, 70 °C; d) *N*,*N*-diethylthiobarbituric acid, 2,2,6,6-tetramethylpiperidine, toluene, reflux; e) 1. $Me_3O^+BF_4^-$, CH_2Cl_2, 0 °C, 2. piperidine, Et_3N, pyridine, reflux, 3. $NaClO_4$; f) piperidine, NaH, MeCN, 70 °C.

The aromatic ketones of the "heptamethine series" bearing three rigidified C=C (double) bonds (Scheme 4) **18a**–**e** were obtained (14 to 50 %) and transformed to **19a**–**e** in 19–76 % yield, in a similar fashion to the above-mentioned dyes. (The dyes **18a**,**b** and **19a**,**b** contain no electron-donating amino group and are hence not true merocyanines. For this reason only the UV/Vis absorption spectra and ^{13}C NMR spectra of these very weakly polarised dyes are considered in this work.) The vinylogous amide **20** (prepared from the triflate **12b** and piperidine in 31 % yield) is stable, in contrast to the analogous *N*,*N*-diethylamino derivative,[8] and was converted both to the merocyanine **21** by reaction with *N*,*N*-diethylthiobarbituric acid (63 %) and to the cyanine **22** by *O*-methylation[29] and subsequent substitution with piperidine.

Experimental determination of the electrical and (non)linear optical properties: In the following, a short survey covers the investigated properties and the experimental methods beyond the routine procedures employed in this work. It is restricted to the expressions for the optical properties and the sources of the crucial quantities. The theoretical background, the experimental procedure and details of evaluation can be found in more detail in the references given.

Ground- and excited-state dipole moments: The polarisation of the electronic ground state of the molecules is expressed by their ground-state dipole moment (μ_g). This and the photo-induced change of dipole moment ($\Delta\mu$) are derived from electro-optical absorption (EOA) spectra of the compounds in 1,4-dioxane. It is assumed that the chromophores can be treated as linear structures in which the ground-state dipole moment, the dipole difference and the transition dipole moment are essentially parallel. This assumption is largely confirmed by the EOAM results. Details of the EOAM experiment and its evaluation have been published in more specialised papers.[30] Integration of the UV/Vis spectrum of the chromophores yields, in addition to the ground and excited-state dipole moment, the magnitude of the transition dipole moment (μ_{eg}).[30d] The dipole difference and the transition dipole may be used to classify the chromophores within a simple two centre CT model.[17] This model is determined by two parameters. The first is the resonance parameter c^2, which measures the contributions of the zwitterionic state relative to the neutral state. Possible values range from $c^2 \approx 0$ ("polyene") through $c^2 \approx 0.5$ ("cyanine") to $c^2 \approx 1.0$ ("betaine") as described above. The resonance parameter may be calculated according to Equation (2):[17]

$$c^2 = 1/2[1 - \Delta\mu(4\mu_{eg}^2 + \Delta\mu^2)^{-1/2}] \quad (2)$$

The second model parameter is the maximal hypothetical dipole difference ($\Delta\mu_{max}$), that is, the difference of the dipole moments of the neutral and the zwitterionic structure, which is proportional to the distance of charge separation. Therefore $\Delta\mu_{max}$ may be regarded as a measure of the effective CT length of the push–pull substituted π system. It may be estimated according to Equation (3).

$$\Delta\mu_{max} = \Delta\mu/(1 - 2c^2) \quad (3)$$

We are aware of the crude character of this model. It provides, however, a very convenient way to classify the chromophore character, and a strong correlation of the c^2 parameter with other experimental observables such as BLA or NMR shifts has been observed.[31]

First- and second-order polarisability: For "one-dimensional" chromophores consisting of a donor and an acceptor group at the terminal positions of a linearly conjugated π system, the static values of the anisotropy of the first- ($\delta\alpha_0$) and second-order polarisability (β_0) can be approximated according to the perturbational two-level model from the transition dipole (μ_{eg}), the wavelength of optical excitation (λ_{eg}) and $\Delta\mu$ [Eqs. (4) and (5)], which have been obtained from UV/Vis spectroscopy and EOAM (vide supra):[32, 33]

$$\delta\alpha_0 = 2\mu_{eg}^2\lambda_{eg}/(hc) \quad (4)$$

$$\beta_0 = 6\mu_{eg}^2\Delta\mu\lambda_{eg}^2/(hc)^2 \quad (5)$$

0947-6539/02/0807-1576 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 7

From the polarisabilities, the above-mentioned FOMs for the different applications can be obtained. The Pockels FOM [Eq. (6); with M = molar mass] is suitable for evaluating chromophores for linear electro-optic devices that are based upon electric-field-dependent refractive index modulation, a pure second-order nonlinear optical effect:

$$F_0^{\text{Pockels}} = \mu_g\beta_0/M \tag{6}$$

Within the Kerr FOM [Eq. (7)] an additional term containing the first-order polarisability anisotropy ($\delta\alpha_0$) appears:

$$F_0^{\text{Kerr}} = 1/M[9\mu_g\beta_0 + 2\mu_g^2\delta\alpha_0/(kT)] \tag{7}$$

This term exceeds the $\mu_g\beta_0$ contribution within strongly polarised neutrocyanines that exhibit both large μ_g and large $\delta\alpha_0$ values. Such chromophores were shown to be promising chromophores for photorefractive materials because of a modulated birefringence caused by the so-called "orientational enhancement effect".[13, 33, 34] The experimental errors of all data obtained from EOA experiments are $<5\,\%$.

Third-order polarisability: The determination of the effective molecular third-order polarisability ($|\gamma_{\text{eff}}|$) was carried out in chloroform. For several concentrations of each dye in the solvent, the nonlinear optical susceptibility $|\chi^{(3)}|$ was determined by time-resolved degenerate four-wave mixing (DFWM) at an off-resonant wavelength (1064 nm). The concentration dependence of $|\chi^{(3)}|$ yields the magnitude of γ relative to the magnitude of $\chi_0^{(3)}$, and the relative phase between γ and $\chi_0^{(3)}$ [Eq. (8)]:

$$|\chi^{(3)}(N)| = |F_\omega^4\,\gamma N + \chi_0^{(3)}| \tag{8}$$

where N denotes the number of molecules per unit volume, $\chi_0^{(3)}$ the nonlinear susceptibility of the solvent and $F_\omega = [n^2(\omega)+2]/3$ is the local field factor according to the commonly applied Lorenz–Lorentz correction, leading to the corrected values ($|\gamma_{\text{LL}}|$). In particular, if γ is in phase with $\chi_0^{(3)}$, the concentration dependence must be linear; if it has the opposite phase, the susceptibility of the solution reaches zero at a finite concentration. The DFWM experiment was realised in a folded-box CARS (coherent anti-Stokes Raman scattering) geometry. The timing of the probe beam versus the pump beams was varied for time-resolved measurements. However, no relaxation processes could be observed, that is, the dominating relaxation processes occurred in the sub-picosecond regime or faster.[35] The experimental errors normally range from 4–13 %; very weak third-order polarisabilities cause errors of 20–62 %. The absolute values for γ were calculated assuming $\chi_0^{(3)} = 6.24\times10^{-22}\,\text{m}^2\,\text{V}^{-2}$ for chloroform.[36]

Vibrational molecular third-order polarisability: Measurements of absolute Raman intensities (I_k) of the kth normal mode at the frequency ω_k of the (mero)cyanines were carried out in chloroform ($10^{-2}\,\text{mol}\,\text{L}^{-1}$). From these a mean value of the various components of γ^{vib} can be obtained [Eq. (9)]. The experimental errors can be estimated to be approximately 30 %.[37]

$$\gamma^{\text{vib}} = \frac{1}{15}\frac{1}{4\pi^2c^2}\sum_k\frac{I_k}{\omega_k^2} \tag{9}$$

Discussion

Linear absorption and fluorescence properties: According to the length of the rigidified polymethine unit and the nature of the donor and acceptor groups, the merocyanines can be divided into the following four subgroups:

1) Dyes **15** and **16** (the pentamethine series containing two rigidified C=C bonds and bearing *p*-*N*,*N*-dialkylaminoaryl donor groups) with absorption maxima in the range from 398 to 568 nm (Table 1).
2) Their higher homologues (heptamethine series) **18c–e** and **19c–e** (absorption maxima between 412 and 582 nm).
3) The "heptamethines" **18a**,**b** and **19a**,**b** that contain *p*-*n*-butyl-substituted (hetero)aromatic donor groups (which are not true merocyanines because of the lack of a nitrogen-containing donor group; 362 to 486 nm).
4) The merocyanines **20**, **17**, **21** and **23** with the nitrogen tethered directly to the rigidified polymethine unit (402 to 648 nm).

With the exception of the last three mentioned molecules all of the foregoing have broad and intense CT-bands (Figures 1 and 2; **18a–e** and **20** not shown).

Within the pairs of two homologous dyes from the first two groups, lengthening of the polymethinic unit causes a moderate bathochromic shift of the absorption maximum (14 to 28 nm; $CHCl_3$). In contrast, a shift of 94 nm is observed for **17** and **23**, which is very similar to the so-called 100 nm

Table 1. Absorption solvatochromism of the (mero)cyanines **15–23** at 298 K; λ_{max} [nm] ($\varepsilon_{\text{max}}\times10^{-3}$ [$\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$]); normalised E_T^N values of the solvents in parentheses.[38]

	toluene [0.099]	chloroform [0.259]	dichloromethane [0.309]	acetonitrile [0.460]	methanol [0.762]
15a	398 (37.6)	416 (37.3)	410 (37.6)	404 (38.3)	422 (36.8)
15b	428 (36.6)	444 (23.6)	440 (34.7)	432 (34.3)	454 (32.5)
16a	504 (51.2)	520 (51.7)	518 (50.0)	510 (48.6)	518 (51.2)
16b	540 (46.0)	568 (48.2)	564 (47.2)	560 (42.8)	568 (47.9)
17	488 (70.6)	494 (121.3)	494 (135.8)	490 (151.6)	490 (162.9)
18a	362 (46.6)	372 (49.1)	368 (49.7)	362 (50.8)	374 (48.2)
18b	394 (45.4)	402 (48.9)	398 (48.9)	390 (48.8)	400 (48.6)
18c	412 (41.9)	424 (43.7)	420 (45.6)	412 (43.5)	426 (41.6)
18d	422 (46.3)	440 (51.6)	434 (46.2)	426 (46.2)	444 (45.2)
18e	450 (40.8)	464 (40.9)	460 (40.4)	450 (38.5)	468 (39.4)
20	402 (42.3)	428 (47.7)	434 (45.2)	424 (44.8)	–[a]
19a	448 (58.5)	454 (60.6)	452 (60.1)	444 (59.5)	448 (62.4)
19b	476 (57.3)	486 (61.6)	480 (61.4)	472 (61.3)	474 (60.8)
19c	510 (52.7)	524 (53.4)	520 (52.2)	510 (47.4)	516 (48.9)
19d	526 (50.0)	548 (57.2)	544 (57.5)	534 (56.8)	538 (55.6)
19e	558 (53.0)	582 (53.7)	578 (49.2)	568 (49.0)	–[b]
23	534 (66.7)	588 (106.5)	588 (128.6)	586 (161.7)	588 (201.8)
21	640 (153.3)	648 (256.4)	644 (238.6)	628 (112.5)	538 (48.2)
22	–[b]	540 (228.8)	540 (283.2)	534 (231.5)	534 (258.5)

[a] Decomposition? [b] Not soluble enough.

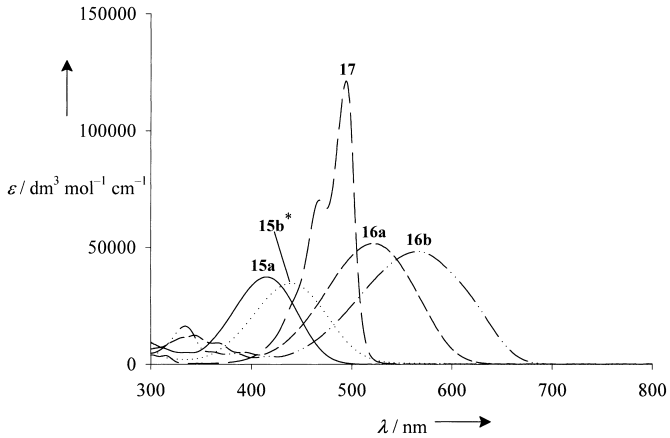


Figure 1. Absorption spectra of the merocyanines **15**–**17** in chloroform (* in dichloromethane) at 298 K.

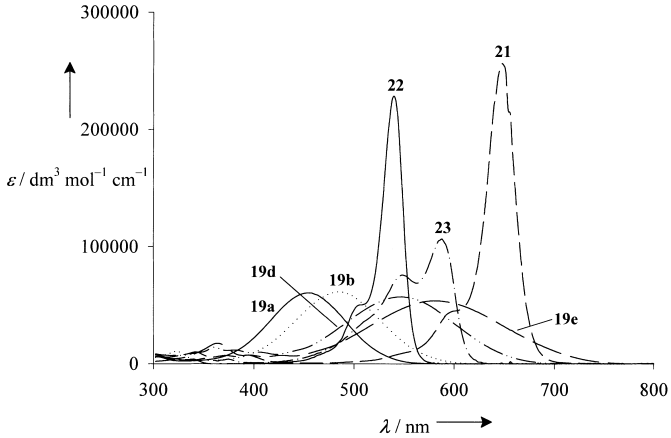


Figure 2. Absorption spectra of the merocyanines **19a**,**b**,**d**,**e**, **21**, **23**, and the cyanine **22** in chloroform at 298 K.

"vinylidene shift" within the homologous series of symmetric cyanine dyes.

The difference between the *p*-*N*,*N*-dialkylaminoaryl donor groups can be evaluated by a comparison of related compounds (i.e. with the same length of the rigidified polymethine unit and the same acceptor). The piperidinothienyl derivatives **15b**, **16b**, **18e** and **19e** exhibit absorption maxima at slightly longer (28 to 58 nm; $CHCl_3$) wavelengths than their dialkylanilino analogues **15a**, **16a**, **18c**, **18d**, **19c** and **19d**. On the other hand, they show smaller molar extinction coefficients (ε). While the first effect—caused by the superior donor character—is a result of the better electronic transmittance of the heteroaromatic unit, because of its smaller loss of aromatic stabilisation upon charge separation, the second is probably due to the weaker overlap of the lone pair within the more pyramidalised nitrogen atom of the piperidino group, in contrast to the nearly planar dimethylamino group[12, 39] with the polymethinic orbitals.

Exchange of the keto group for the dicyanomethylene acceptor group means both introduction of a stronger acceptor and also lengthening of the chromophore by two π electrons.[3b] This leads to stronger bathochromic shifts than the above-mentioned change of the donor group (vide supra). While the piperidinothienyl derivatives (vide supra) are affected more strongly (118 to 124 nm; $CHCl_3$) than the dialkylanilino dyes (100 to 108 nm; $CHCl_3$) no significant difference is observed between the *p*-alkylaryl donors (third group). The strongest influence of increasing acceptor strength is observed within the fourth group. Introduction of the dicyanomethylene and the *N*,*N*-diethylthioxodihydropyrimidinedionylidene (diethylthiobarbituric acid; $+6$ π electrons) acceptor group leads to bathochromic shifts of 160 and 220 nm, respectively, and dramatic changes in band shape, which will be discussed below.

The solvent dependence of absorption behaviour of the dyes within the first three groups and also of **20** is very similar, with positive solvatochromism going from the apolar toluene to solvents of medium polarity (chloroform and dichloromethane), then negative shifts on going to the more polar acetonitrile and positive again on turning to a polar protic medium (methanol). In general, the solvatochromic shifts are rather small, ranging from maximum of 12 nm within the third group and maximum of 28 nm within the first and second group, and no change in band shape can be observed. In contrast, the dyes **17**, **21** and **23** of group four exhibit only small shifts of the position of the absorption maxima but large changes in band shape with increasing solvent polarity.

While the cyanine character (a sharp and very intense absorption with a steep descent of the long wavelength flank) of the absorption band of **23** increases with solvent polarity (Figure 3) a cyanine-like behaviour is observed for **21** even in a solvent of only medium polarity (chloroform, Figure 4). Solvents of greater or of lesser polarity lead to a loss in cyanine character. (Similar results to those for **23** are obtained for its lower homologue **17**).

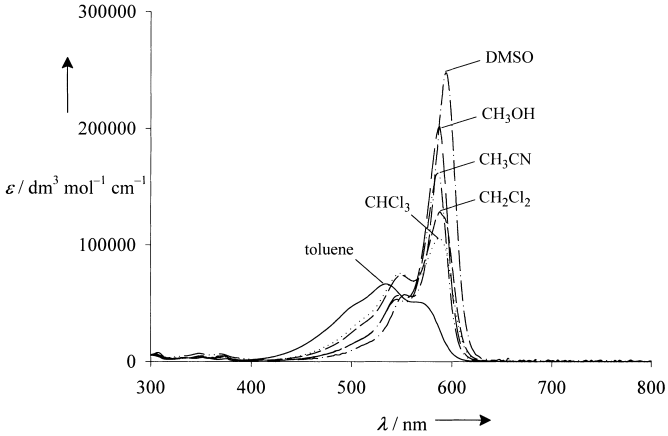


Figure 3. Absorption solvatochromism of the merocyanine **23** at 298 K.

It was reported for merocyanines similar to **16a** and **19c**,**d** that the rigidified forms exhibit slightly blue-shifted absorption bands relative to their open-chain analogues.[11] This was confirmed by our findings both for the above-mentioned dyes and for **15a** and **16a**, by comparison with data from the literature for the non-rigidified molecules.[40] The hypsochromic shifts range from 17 to 23 nm in $CHCl_3$, and no marked effects of chain length and the nature of the acceptor group

  0947-6539/02/0807-1578 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 7

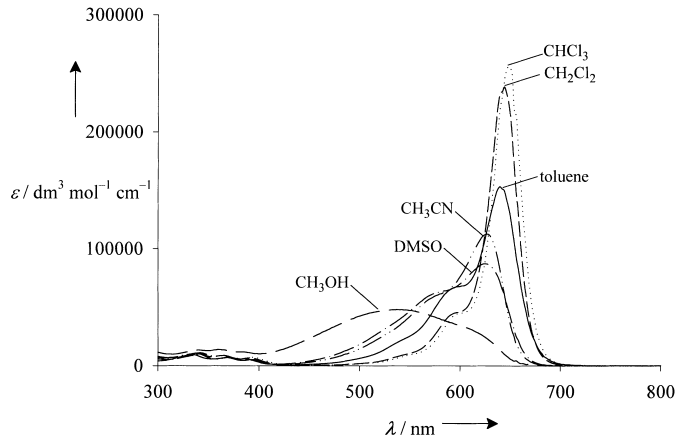


Figure 4. Absorption solvatochromism of the merocyanine **21** at 298 K.

Table 2. Fluorescence properties of the merocyanines **15**–**17**, **18d**,**e**, **19d**,**e**, **20**, **21** and **23**, and the cyanine **22** in chloroform at 298 K ($c = 10^{-5}$ mol L^{-1}).

	λ_{fl} [nm]	$\lambda_{fl} - \lambda_{abs}$ [nm]	η_{fl} [%][a]
15a	532	116	65
15b	564	118	50
16a	635	113	28
16b	669	103	36
17	507	12	1
18d	601	177	48
18e	644	180	20
20	507	79	52
19d	715	167	15
19e	759	177	8
23	604	16	23
21	670	22	11
22	553	13	88

[a] Fluorescence standard: Rhodamine 6G, except for **21**, for which Rhodamine 700 was used.

could be observed. In contrast, the merocyanines of the fourth group exhibit red-shifted absorption bands with respect to the analogous (or comparable) open chain compounds (in $CHCl_3$).[41] A neglible bathochromic shift is observed for **20** (6 nm); this is clearly different from its "phenylogues" **16c**,**d**. The partly cyanine-like dyes **17** (18 nm) and **23** (38 nm) show pronounced red shifts and, in addition, an increase of the bathochromic effect of rigidification with increasing chain length. The absorption band of the cyanine **22** is also bathochromically shifted (ca. 16 nm; in MeOH) relative to its non-rigidified counterpart (in EtOH).[39] The latter can easily be explained with the help of the common colour rules for cyanine dyes.[42] (The "unexpected" electron-withdrawing nature of the aliphatic substituents that are part of the ring system, compared with that of the hydrogens in simple streptomethines, is reflected in the downfield-shifted signals of the atoms C-2, C-7, C-8a, and C-9a in the ^{13}C NMR spectrum of **22** relative to those of the analogous positions in 2,7-bis(dimethylamino)heptamethinium chloride.[43]) The different influences of the substituted polymethinic moiety on the absorption spectra of the merocyanines will form the subject of forthcoming studies.

The fluorescence of the (mero)cyanines **15**–**17**, **18d**,**e**, **19d**,**e** and **20**–**23** was investigated in chloroform (Table 2). The dyes of the heptamethine series (second group) exhibit, in general, larger Stokes shifts (167 to 180 nm compared with 103 to 118 nm), but smaller quantum yields (8 to 48 % compared with 28 to 65 %) than their pentamethine counterparts. Whereas the di-*n*-butylanilino-substituted heptamethines **18d** and **19d** show markedly higher quantum yields (η_{fl}) than the piperidinothienyl derivatives **18e** and **19e**, no corresponding trend could be observed within the pentamethine series. The cyanine-like character of the merocyanines **17**, **21** and **23** is reflected in the smaller stokes shifts (12 to 22 nm), but only weak to medium values for η_{fl} were found. Interestingly a large difference in η_{fl} between the homologues **17** and **23** was observed (1 and 23 %). Nevertheless only the cyanine **22** shows a remarkably high quantum yield.

Polarisation: The extent of the contribution of the charge-separated resonance form (**C**) on the electronic ground state of the molecules is reflected in their increasing ground-state dipole moment (μ_g; Table 3), which is clearly affected by the length of the polymethinic unit and the donor and acceptor.

The ketones **15a**,**b** and the methanedicarbonitriles **16a**,**b** of the pentamethine series exhibit nearly the same values as their higher homologues **18c**,**e** and **19c**,**e**, respectively, because for a given pair of donor and acceptor groups an increase of the conjugation length renders charge separation

Table 3. Optical and electric properties of the merocyanines **15**–**17**, **18c**,**e**, **19c**,**e**, **20**, **21** and **23** obtained from EOAM in 1,4-dioxane solution at 298 K.

		15a	**15b**	**16a**	**16b**	**17**	**18c**	**18e**	**20**	**19c**	**19e**	**23**	**21**
M	[g mol^{-1}]	351.53	313.46	399.58	361.50	279.38	319.45	365.54	283.41	367.49	413.59	331.46	465.66
λ_{max}	[nm]	395	425	498	534	487	410	447	403	504	549	533	638
ε_{max}	[dm^3 mol^{-1} cm^{-1}]	38000	34100	50600	46200	79800	42600	40800	45100	55200	51600	48300	179700
μ_{eg}	[10^{-30} C m]	27	26	33	33	32	30	30	30	37	38	31	43
μ_g	[10^{-30} C m]	19	18	30	31	38	20	20	25	30	32	42	45
$\Delta\mu$	[10^{-30} C m]	55	49	68	69	8	53	51	50	67	72	40	17
$\Delta\mu_{max}$	[10^{-30} C m]	77	71	95	95	64	80	79	78	100	105	74	88
c^2		0.14	0.16	0.14	0.14	0.44	0.17	0.18	0.18	0.16	0.15	0.23	0.40
$\delta\alpha_0$	[10^{-40} C V^{-1} m^2][a]	33	29	55	59	50	37	42	36	70	78	52	118
β_0	[10^{-50} C V^{-2} m^3][b]	95	91	279	326	30	122	144	109	353	461	169	191
$F_0^{Pockels}$	[10^{-76} C^2 V^{-2} m^4 kg^{-1} mol]	0.51	0.53	2.10	2.79	0.40	0.76	0.78	0.97	2.92	3.55	2.12	1.86
F_0^{Kerr}	[10^{-74} C^2 V^{-2} m^4 kg^{-1} mol]	0.19	0.19	0.79	1.01	1.30	0.29	0.29	0.47	1.11	1.24	1.52	2.70

[a] 10^{-40} C V^{-1} m^2 = 0.8988 × 10^{-24} esu. [b] 10^{-50} C V^{-2} m^3 = 2.694 × 10^{-30} esu.[1]

more difficult. Within the derivatives bearing the piperidino donor tethered directly to the polymethinic chain (**20**, **17** and **23**), the shortening of the chromophore relative to the corresponding *N*,*N*-dimethylanilino- and piperidinothienyl derivatives **18c**,**e**, **16a**,**b** and **19c**,**e** is more than compensated by the gain in donor strength as a result of the loss of the aromatic "hurdle". Hence, larger μ_g values are found here than for the corresponding "aromatic" dyes. The sequence of merocyanines according to increasing ground-state polarisation based upon these values is used for the discussion of the NMR data.

The large increase of dipole moment upon optical excitation ($\Delta\mu$) observed for all dyes (with the exception of **17**, **21** and **23**) is evidence for their marked oligoene-like character. This is also expressed by their small c^2 resonance parameters, which lie in the range 0.14–0.18. The dependence of $\Delta\mu$ on the nature of the endgroups and the length of the polymethinic chain is rather similar to that of μ_g (vide supra). Interestingly, the piperidinothienyl-substituted ketones **15b** and **18e** exhibit smaller $\Delta\mu$ values than the corresponding anilino derivatives **15a** and **18c**, respectively. This effect is more marked within the pentamethines and might be due to a partial compensation of the better "electronic" donor character by the more angular geometry of the heteroaromatic donor group, which becomes more significant with decreasing chromophore length and acceptor strength. In contrast to the oligoene-like dyes, markedly reduced $\Delta\mu$ and increased c^2 values are observed for **23**, **17** and **21**; this indicates their moderate (**23**) or pronounced cyanine-like character (**17** and **21**). The heptamethine **21** is polarised close to the cyanine limit ($c^2 = 0.40$) even in the rather apolar solvent 1,4-dioxane; this was expected from its absorption spectra (Figure 4). The strong dependence of the extent of charge separation on the intramolecular distance between the donor and acceptor is reflected in the homologous pair **17** and **23**. The pentamethine derivative **17** is distinctly more cyanine-like ($c^2 = 0.40$) than its heptamethinic counterpart **23** ($c^2 = 0.23$).

First- and second-order polarisabilities: As described above, the anisotropy of the first- ($\delta\alpha_0$) and second-order polarisability (β_0) may be estimated from the EOAM data (Table 3, Figures 5 and 6).

Within the pentamethine and heptamethine series the values of the dyes bearing aromatic donor groups (**15a**,**b**, **16a**,**b** and **18c**,**e**, **19c**,**e**, respectively) show the expected increase with increasing donor and acceptor strength of the endgroups, with the above-mentioned exception for **15b**. As expected large β_0 values were obtained for **19c** ($353 \times 10^{-50}\,C\,V^{-2}\,m^3$) and for **19e** ($461 \times 10^{-50}\,C\,V^{-2}\,m^3$), which make these dyes suitable for EO-devices, which is also expressed by their Pockels-FOMs. (The use of chromophores such as **16b** and **19c**,**d** in NLO side-chain polyquinolines has been reported previously.)[44] Within the more strongly polarised piperidino derivatives **17**, **23** and **21**, only the last one exhibits a notably high $\delta\alpha_0$ value. As expected, the β_0 values of these partially cyanine-like dyes are comparatively small with respect to the above-mentioned oligoenes. According to its very high Kerr FOM, **21** should be the most promising candidate for the use in photorefractive polymers of this series, but this is probably hampered by its long wavelength absorption. (The successful applications of merocyanines similar to **17** and **23** have been reported.[13, 14])

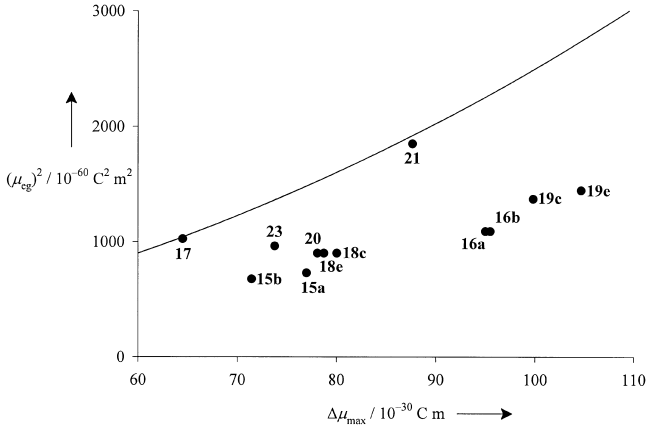


Figure 5. Plot of the reduced linear polarisability $\alpha_0(hc/\lambda_{eg})/2 = \mu_{eg}^2$ as a function of the effective CT dipole length. The solid line represents the theoretical maximum of the two-level CT model.

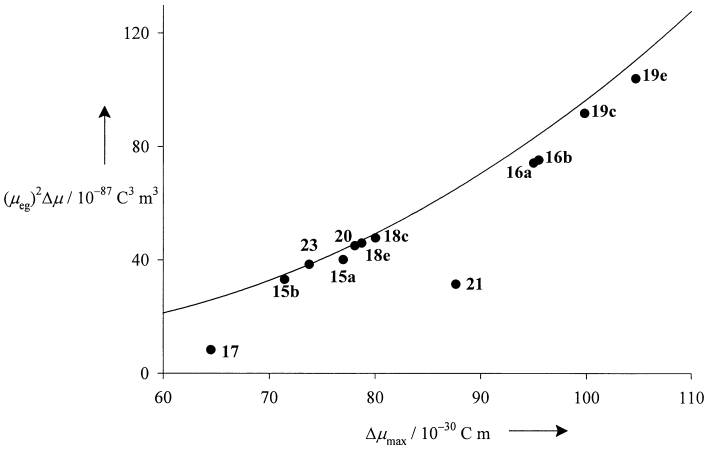


Figure 6. Plot of the reduced second-order polarisability $\beta_0(hc/\lambda_{eg})^2/6 = \mu_{eg}^2\Delta\mu$ as a function of the effective CT dipole length. The solid line represents the theoretical maximum of the two-level CT model.

In Figures 5 and 6, reduced first- and second-order polarisabilities are displayed as a function of the model parameter $\Delta\mu_{max}$, which can be regarded as a measure of the effective CT length of the chromophores. In the reduced polarisabilities, the effects of the transition wavelength are eliminated [see. Eqs. (4) and (5)]. The solid line represents the maximum value of the reduced polarisability that can be achieved for a given conjugation length within the CT model. Figure 5 shows that only the chromophores **17** and **21**, which are polarised close to the cyanine limit, reach the maximum values for the linear polarisability as predicted by the CT model for $c^2 \approx 0.5$. Thus both chromophores optimise this polarisability for their conjugation length. In Figure 6, on the other hand, both chromophores fail to reach the maximum value of the reduced second-order polarisability. This is attributable to the proportionality between the $\Delta\mu$ and β_0 [Eq. (5)], which makes β_0 go to zero at the cyanine limit ($c^2 = 0.5$). All other chromophores are close to the maximum value with their c^2 values ranging

  0947-6539/02/0807-1580 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 7

from 0.14 to 0.27. This is in agreement with the CT model, which predicts the maximum β_0 to be reached with resonance parameters of $c^2 = 0.21$.

Third-order polarisability: The effective third-order polarisabilities obtained directely from DFWM measurements ($|\gamma_{\mathrm{eff}}|$) cover a range of two orders of magnitude for the merocyanines of the pentamethine and heptamethine series and the heptamethine cyanine (Table 4); a very large maximum value for $|\gamma_{\mathrm{eff}}|$ was found for **19d** (548×10^{-60} C V^{-3} m^4). We have also included the values derived from these by Lorenz-type local field correction ($|\gamma_{\mathrm{LL}}|$). A more complete treatment of the local field correction leads to factors that may depend strongly on the solute rather than on the overall refractive index of the solution. Therefore, not only the absolute values, but also the relative magnitudes of γ are influenced by local field corrections.[45]

Table 4. Experimental third-order polarisabilities ($|\gamma_{\mathrm{eff}}|$) of the (mero)cyanines **15**–**17**, **18d**,**e**, **19d**,**e**, **20**–**23**, obtained from DFWM experiments (1064 nm), Lorentz-type corrected third-order polarisabilities ($|\gamma_{\mathrm{LL}}|$) and vibrational third-order polarisabilities ($|\gamma^{\mathrm{vib}}|$) calculated from absolute Raman intensities. All measurements carried out in chloroform at 298 K.

	N π electrons	$\lvert\gamma_{\mathrm{eff}}\rvert$ [10^{-60} C V^{-3} m^4][a]	$\lvert\gamma_{\mathrm{LL}}\rvert$ [10^{-60} C V^{-3} m^4][a]	$\lvert\gamma^{\mathrm{vib}}\rvert$ [10^{-60} C V^{-3} m^4][a]
15a	12	14	5	3
15b	12	71	24	5
16a	14	118	39	24
16b	14	204	68	30
17	10	14	5	4
18d	14	13	4	3
18e	14	395	130	8
19d	16	548	183	41
19e	16	318	106	67
20	10	12	4	3
23	12	109	36	21
21	16	168	56	19
22	10	132	44	4

[a] 10^{-60} C V^{-3} m^4 = 8.078×10^{-36} esu.[1]

For a comparison, the structural differences (e.g., the nature of the donor groups) and the relative lengths of the chromophores should be taken into account. Expressions for the dependence of γ upon the so-called conjugation length of π systems as found in the literature are usually given in form of power-law dependencies, with the number of atomic sites or repeat units within the system as the basis and varying exponents for the different classes of molecules (e.g., oligoenes, merocyanines and cyanines).[46] Though for this reason a general and quantitative standardisation of the γ values of the differently polarised merocyanines and the cyanine is not possible, the number of π electrons within the chromophore can be considered in an approximate way.[3b]

Nevertheless a general dependence of γ upon the differences in ground-state polarisation could not be observed as for the second-order polarisability β: Indeed the value obtained for the relatively weakly polarised merocyanine of the heptamethine series **20** is about one order of magnitude smaller than those of the merocyanines with moderate (**23**) or pronounced (**21**) cyanine-like character, and also of the cyanine **22**. The fact that the γ value of **22** is exceeded by that of **21** must be related to the greater number of π electrons of the latter; this is also reflected in its absorption at longer wavelengths (Table 1). Within the pentamethine series **15a**,**b** and **16a**,**b**, γ increases with increasing donor and acceptor strengths, but an analogous trend is not observed for the higher homologues **18d**,**e** and **19d**,**e**. In addition these last-mentioned oligoene-like heptamethines show larger γ values than their more strongly polarised counterparts **20**–**23**, which cannot be explained by the number of π electrons (cf. **19d**,**e** and **21**). Finally a sign reversal of γ, predicted by the two-level model for push–pull oligoenes for the static γ values (positive for the oligoene-like dyes **15**–**16**, **18**–**20** and negative for the stronger polarised ones **17**, **21** and **23** and the cyanine **22**),[18a] is clearly not observed.

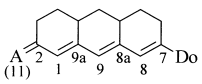
The failure of the two-level model is a clear indication that two-photon-allowed transitions together with the dipolar contribution (the positive channels of γ) dominate over the contribution from the bleaching of the one-photon transition (the negative channel).[47] It should be noted that, as our experiment determines the hyperpolarisabilites $\gamma(-\omega;\omega,-\omega,\omega)$ in the near infrared frequency region, the relative contributions of the different channels of γ are very different from static values or THG (third harmonic generation) measurements.[47] In this context, the decrease of γ from **19d** to **19e** and generally the higher values of the oligoene-like heptamethines relative to the highly polarised heptamethines may be explainable by the anticipated reduction of the dipolar term, leaving only the two-photon term to compete with (and reverse) the negative term. This important result calls for a careful analysis of the energies and transition moments of two-photon-allowed transitions. Measurements on this subject have been performed;[48] a deeper analysis to provide an overall picture is in preparation.

The vibrational third-order polarisabilities $|\gamma^{\mathrm{vib}}|$ were calculated from Raman intensities obtained in the same solvent and display a similar behaviour (Table 4). Because of the fundamental differences in the two experimental methods used, a distinct or even quantitative separation of the vibrational contribution to $|\gamma_{\mathrm{LL}}|$ using the Raman-based $|\gamma^{\mathrm{vib}}|$ cannot be achieved. From a qualitative correlation the following trend is evident: Small $|\gamma^{\mathrm{vib}}|$ values were found for **15a**,**b**, **17**, **18d**, **20** and **22**, which already exhibited small $|\gamma_{\mathrm{LL}}|$. This is independent of the large differences in ground-state polarisation within these molecules. In addition the larger vibrational polarisabilities of **16a**,**b** and **19d** seem to be reflected in the DFWM experiment, but a general coherence is prevented by the thiophene derivatives **18e** and **19e**. This clearly indicates that the nature and interdependence of all quantities contributing to γ obtained from DFWM experiments are more sophisticated.

NMR studies: The extent of ground-state polarisation (or the cyanine-like character) of merocyanines is clearly reflected in the BLA within the polymethinic chain. For this reason the BLA has become a parameter often used for the description of merocyanines in their electronic ground state and it is usually taken directly from X-ray crystallographic analysis or derived from the ^3J(H,H) coupling constants of the vicinal

methinic protons obtained from ^{1}H NMR spectroscopy.[49] The first method suffers from the need for the preparation of single crystals and allows only an observation of the molecule within the rather polar environment of the solid state. The second opens up a broader variation of the surrounding medium by the choice of appropriate solvents and has become a common tool in this field.[50] In contrast, only little work has been published concerning the ^{13}C NMR chemical shifts as a measure of electron density along the polymethinic chain to describe the ground-state electronic structure of merocyanines.[51]

Within the heptamethine series **18**–**21** and **23** and the cyanine **22**, the ^{13}C NMR chemical shifts (Table 5) of the carbon atoms C-*n* of the polymethinic unit along the path C-2 to C-7 (**D**) indicate an alternating charge distribution as expected for cyanines and merocyanines.[52]



18–23

D

Table 5. Selected ^{13}C NMR chemical shifts δ [ppm] of the (mero)cyanines **18**–**23** (100 MHz, $CDCl_3$, 298 K).

	C-11	C-2	C-1	C-9a	C-9	C-8a	C-8	C-7
18a	–	199.9	122.9	159.9	124.7	149.4	124.3	144.3
18b	–	199.8	122.7	159.7	124.5	149.0	122.5	138.5
18c	–	199.9	122.2	160.4	123.4	150.3	121.6	144.5
18d	–	199.8	121.9	160.5	123.0	150.5	120.8	144.5
18e	–	199.8	121.8	160.4[a]	122.8	150.0	119.5	139.2
20	–	199.3	118.0	162.1	115.8	153.5	99.6	154.1
19a	74.6	169.6	119.8	159.0	125.0	153.0	124.4	146.6
19b	74.1	169.4	119.6	158.9	124.7	152.7	122.6	140.7
19c	73.2	169.5	119.0	159.6	123.7	154.2	121.6	147.0
19d	72.7	169.4	118.7	159.7	123.4	154.5	120.9	147.2
19e	72.0	169.1	118.5	159.5	122.9	154.1	119.3	141.9
23	64.2	167.7	113.8	161.5	116.0	160.2	100.0	157.4
21	100.1	165.4	122.5	167.6	120.3	167.7	103.8	161.3
22	–	163.4	102.0	167.1	115.9	167.1	102.0	163.4

[a] Might be C-5′.

To investigate whether increasing polarisation is reflected in the chemical shifts of the methinic carbons within the merocyanines [δ(C-$n_{\text{merocyanine}}$)] in comparison to those obtained for the analogous positions within the cyanine [δ(C-n_{cyanine})], the "δ deviation" ($\Delta\delta$) of each merocyanine carbon atom was calculated (Table 6) according to Equation (10):

$$\Delta\delta = \delta(\text{C-}n_{\text{merocyanine}}) - \delta(\text{C-}n_{\text{cyanine}}) \quad (10)$$

For the sake of comparison from all heptamethines under investigation the acceptor and donor bearing *ipso*-carbons C-2 and C-7 were not taken into account.

With increasing donor strength (i.e., increasing polarisation) a smooth decrease of $|\Delta\delta|$ within the group of the ketones **18** and a more marked decrease in **20** can be observed throughout all carbon atoms (Table 6, Figure 7).

While the values of C-1, C-8 and C-9 fit in this trend exactly, those obtained for C-8a and C-9a differ in that the thienyl-substituted molecules **18b**,**e** exhibit slightly higher (0.1–0.5) $|\Delta\delta|$ values than their phenyl counterparts **18a**,**c**,**d**. The same general trend, as well as the special behaviour of the thiophene derivatives, is observed within the methanedicarbonitriles **19** and **23**. In addition, within a pair of corresponding molecules bearing the same donor, the exchange of the keto for the dicyanomethylene group (e.g. **18a** and **19a**) leads to reduced $\Delta\delta$ values at C-1 about 3.1–3.3 ppm for the "aromatic" derivatives **19** and 4.2 ppm for **23**. (Nevertheless this trend is not continued within the thiobarbituric acid derivative **21**, which is subject to an enhancement of $\Delta\delta$ about 4.5 ppm.) A similar reduction of $|\Delta\delta|$ on introduction of a stronger acceptor can be observed within all merocyanines at C-8a (3.6–4.1 ppm for **19a**–**e** and 6.7 and 14.2 ppm for **23** and **21**, respectively), while comparatively small enhancements of about 0.8–0.9 ppm (**19a**–**e**) and 0.6 ppm (**23**) and a remark-

Table 6. Deviation of the ^{13}C NMR chemical shifts $\Delta\delta$ [ppm] of the methinic carbons of the merocyanines **18a**–**e**, **19a**–**e**, **20**, **21** and **23** relative to the cyanine **22** (100 MHz, $CDCl_3$, 298 K) [Eq. (10)].

	C-2	C-1	C-9a	C-9	C-8a	C-8	C-7
18a	36.5	20.9	–7.2	8.8	–17.7	22.3	–19.1
18b	36.4	20.7	–7.4	8.6	–18.1	20.5	–24.9
18c	36.5	20.2	–6.7	7.5	–16.8	19.6	–18.9
18d	36.4	19.9	–6.6	7.1	–16.6	18.8	–18.9
18e	36.4	19.8	–6.7	6.9	–17.1	17.5	–24.2
20	35.9	16.0	–5.0	–0.1	–13.6	–2.4	–9.3
19a	6.2	17.8	–8.1	9.1	–14.1	22.4	–16.8
19b	6.0	17.6	–8.2	8.8	–14.4	20.6	–22.7
19c	6.1	17.0	–7.5	7.8	–12.9	19.6	–16.4
19d	6.0	16.7	–7.4	7.5	–12.6	18.9	–16.2
19e	5.7	16.5	–7.6	7.0	–13.0	17.3	–21.5
23	4.3	11.8	–5.6	0.1	–6.9	–2.0	–6.0
21	2.0	20.5	0.5	4.4	0.6	1.8	–2.1

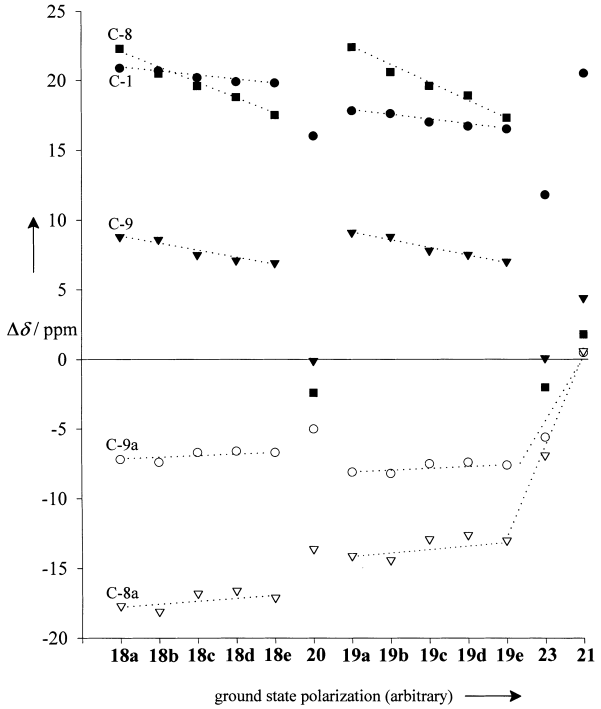


Figure 7. Deviations of the chemical shifts $\Delta\delta$ [Eq. (10)] of selected methinic carbons within the merocyanines **18**–**21** and **23** relative to the analogous positions within the cyanine **22**, arbitrarily correlated to their relative ground-state polarisation (the dotted lines are only guides to the eye).

  0947-6539/02/0807-1582 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 7

able decrease of about 5.5 ppm (**21**) are seen at C-9a. In contrast, $\Delta\delta$ at C-8 and C-9 are essentially unaffected by increasing acceptor strength. Furthermore, it can be seen that the distribution of electron density becomes more and more symmetric within the central part of the polymethinic unit along C-8a, 9, 9a in **23** and **21** relative to **19a–e** (Tables 5 and 6) and in addition $\Delta\delta$ nearly vanishes for **21** at C-8a and C-9a. Since the electronic symmetry clearly reflects the cyanine-like electronic ground state of the hexatriene unit within a molecule, the development of $\Delta\delta$ with increasing polarisation leads to the assumption that the dependency of both quantities is displayed at one of the last two mentioned carbons. Though the same trend (decreasing $|\Delta\delta|$ with increasing polarisation corresponding to growing donor strength within the ketones **18** and **20** on the one hand and the methanedicarbonitriles **19** and **23** on the other) is observed within each of the two mentioned groups at C-9a, increasing acceptor strength within the above-mentioned pairs of corresponding molecules (e.g. **18a** and **19a**, vide supra) drives $|\Delta\delta|$ in the opposite direction. For this reason $|\Delta\delta|$ at C-9a does not turn out to be an indicator of ground-state polarisation.

Finally all these aspects have to be considered at C-8a: The general decrease of $|\Delta\delta|$ within both groups (**18** and **19**) as well as the slightly smaller absolute values of **19** reflect the gradually increasing polarisation of these oligoene-like merocyanines (vide supra for the special features of the thiophene derivatives). As expected, the value for **20** is markably reduced relative to all the aromatic ketones **18**, but still somewhat larger than those for **19c–e**. The fact that $|\Delta\delta|$ is distinctly reduced in the case of **23** and almost vanishes for **21** corresponds to the moderate or pronounced cyanine-like character of these dyes compared to all of the others, as was already demonstrated by their different shape of their absorption spectra. Hence, increasing strengths of both the donor and the acceptor group has a consistent influence on the ^{13}C NMR chemical shift at this position. The better comparability of C-8a than of C-9a within the merocyanines and the cyanine could be clearly explained by its lower spatial distance from the donor group, which becomes exactly the same (piperidino) in **23** and **21** as in the cyanine.

In conclusion the increasing polarisation of merocyanines derived from the rigidified hexatriene unit seems to be reflected in the NMR chemical shift of C-8a; the γ atom with respect to the donor group. The $\Delta\delta$ parameter as an approximation can be used both for the weakly polarised oligoene-like merocyanines bearing different (hetero)aromatic donor groups and for the more strongly polarised cyanine-like systems without aromatic moieties within the chromophore. $\Delta\delta$ ranges from large negative values (−18.1 ppm for the oligoene **18b**) to values near zero (0.6 ppm for the nearly cyanine-like dye **21**). From this it could be assumed that a merocyanine of the type considered here polarised exactly to the cyanine limit, should exhibit the same chemical shift ($\Delta\delta = 0$) at C-8a as the symmetric cyanine in the same solvent. Consequently stronger polarisation beyond the cyanine limit would lead to positive values. Though the last point would seem to be easily investigated by determination of $\Delta\delta$ for **23** and **21** in a variety of more polar solvents (see Figures 3 and 4), their insufficient solubility meant that the data could be only obtained in DMSO solution (Table 7). Unfortunately no exact assignment of the signals of the quaternary carbons by using two-dimensional NMR spectrosocpy was possible.

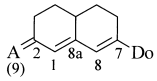
Table 7. Observed ^{13}C NMR chemical shifts δ of the methinic carbons of the merocyanines **21** and **23** (100 MHz, [D6]DMSO, 298 K). The deviations relative to C-8 of the cyanine **22** $\Delta\delta$ [ppm] are given in parentheses [Eq. (10)].

23	164.7	164.2	162.1	161.3
	(−1.4)	(−1.9)	(−4.0)	(−4.8)
21	168.6	168.4	162.2[a]	156.7[b]
	(2.5)	(2.3)	(−3.9)	(−9.4)

[a] Probably C-2. [b] Probably C-7.

Therefore no direct evidence for the expected increased cyanine-like character of **23** in DMSO (symmetric distribution of charge density along C-8a, 9, 9a and markedly reduced (<6.9) values for $|\Delta\delta|$ at C-8a) could be observed. Nevertheless the second requirement is fulfilled by any possible assignment with $\Delta\delta$ values ranging from −4.8 to −1.4 ppm. Similar results were obtained for **21**, which exhibits partially betaine-like character in DMSO: Two of three possible assignments reach the required value of $\Delta\delta > 0.6$ ppm (Table 7).

In a further study the NMR chemical shifts (Table 8) of the methinic carbons within the pentamethine series **15–17** [δ(C-n_{pent})] were compared to those at the corresponding positions within their higher homologues **18d,e**, **19d,e** and **23** [δ(C-n_{hept})] by using a $\Delta\delta'$ [Eq. (11)] similar to that mentioned above (**E**; Table 9):



15–17

E

$$\Delta\delta' = \delta(\text{C-}n_{pent}) - (\text{C-}n_{hept}) \quad (11)$$

A relatively good agreement, with $\Delta\delta'$ ranging from −1.2 to 0.5 ppm, was observed at C-1, C-2 and C-8 (Table 9). In

Table 8. Selected ^{13}C NMR chemical shifts δ of the merocyanines **15–17** (100 MHz, $CDCl_3$, 298 K).

	C-9	C-2	C-1	C-8a	C-8	C-7
15a	–	200.0	122.3	160.3	120.3	148.3
15b	–	199.6	121.7	159.9	118.3	142.7
16a	72.9	169.9	119.0	159.7	120.2	152.0
16b	71.2	169.1	118.0	159.2	118.2	146.5
17	61.6	167.8	111.3	163.7	99.6	160.2

Table 9. Deviation of the ^{13}C NMR chemical shifts $\Delta\delta'$ [ppm] of the methinic carbons of the merocyanines **15a,b**, **16a,b** and **17** relative to their higher homolgues **18d,e**, **19d,e** and **23** (100 MHz, $CDCl_3$, 298 K) [Eq. (11)].

	C-9[a]	C-2	C-1	C-8a	C-8	C-7	δ(C-8a$_{pent}$)-δ(C-9a$_{hept}$)
15a	–	0.2	0.4	9.8	−0.5	3.8	−0.2
15b	–	−0.2	−0.1	9.9	−1.2	3.5	−0.5
16a	0.2	0.5	0.3	5.2	−0.7	4.8	0.0
16b	−0.8	0.0	−0.5	5.1	−1.1	4.6	−0.3
17	−2.6	0.1	−0.5	3.5	−0.4	2.8	2.2

[a] Denoted C−11 within **19d,e**, and **23**.

contrast, significant deviations are found at C-7 and C-8a. While the effect at C-7 is slightly more pronounced within the methanedicarbonitriles **16**, remarkably larger $\Delta\delta'$ values are caused by the keto group at C-8a within **15**. The absolute values obtained for **17** are smaller, but their relative sizes fit the trend observed for **16**. Because of its central position within the polymethinic unit of the pentamethines, C-8a is of special interest. Though the largest deviations from the analogous position within the heptamethines are found here, a remarkable similarity to the position C-9a of those is evident (at least in **15** and **16** with $\Delta\delta'$ ranging from -0.5 to 0.0 ppm). This demonstrates that the acceptor groups cause a more far-reaching effect on the electronic structure from the end to the middle of the polymethinic unit than the donor groups in weakly polarised oligoene-like merocyanines.

The signal of C-9 (the central carbon atom within the dicyanomethylene acceptor group; C-11 within the heptamethines) exhibits nearly the same chemical shift within the two *p*-*N*,*N*-di-*n*-butylanilino derivatives **16a** and **19d**, but it shows a significant highfield shift within the pentamethines, considering the pairs **16b**/**19e** and **17**/**23**, which increases with growing donor strength. This is evidence for a comparatively larger contribution of the zwitterionic form to the electronic ground state in the pentamethines, which can be explained by the facilitated charge separation over shorter intermolecular distances.

Conclusion

An efficient six-step synthesis of the precursors of donor–acceptor oligoenes with three sterically fixed all-*trans* C=C bonds is presented. Oligoene-like to cyanine-like ground-state polarisation of the dyes was attained by appropriate endgroups. High static second- (β_0) and third-order polarisabilities ($|\gamma_{LL}|$) were found within oligoene-like merocyanines (**19c**: $\beta_0 = 951 \times 10^{-30}$ esu; **19d**: $\gamma_{LL} = 15 \times 10^{-34}$ esu; **19e**: $\beta_0 = 1242 \times 10^{-30}$ esu, $\gamma_{LL} = 9 \times 10^{-34}$ esu), which exceed the $|\gamma_{LL}|$ values obtained for a merocyanine polarised to the cyanine-limit and for a cyanine. These unexpected results obtained by DFWM are probably due to two-photon-allowed transitions and vibrational contributions. The latter is corroborated by the calculated vibrational third-order polarisabilities. The differences of the ^{13}C NMR chemical shifts at the γ-position (with respect to the donor group) within the hexatriene unit of the merocyanines, compared to those obtained for the analogous position within a corresponding cyanine, decrease with increasing ground-state polarisation. This $|\Delta\delta|$ parameter can be taken as an approximate measure of the extent of cyanine-like character of these merocyanines in their electronic ground state. The distribution of electron density within the polymethinic unit is more strongly affected by the acceptor than by the donor group, as can be seen from a comparison of the ^{13}C NMR chemical shifts of donor–acceptor hexatrienes with their lower homologues.

Experimental Section

General: All solvents were purified by distillation before use and anhydrous solvents were obtained using common methods. Flash chromatography was performed over silica gel "Kieselgel 60" (0.040–0.063 mm, Merck). Melting points were determined on a MEL-Temp II, Laboratory devices, USA or on a Kofler hot stage microscope apparatus, Reichert (Austria), and are uncorrected. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra were run on a Bruker AM400 and Bruker Avance DRX400 instrument in $CDCl_3$ (^{1}H) or the solvent (^{13}C) as internal standards) or [D$_6$]DMSO (solvent (^{1}H and ^{13}C) as standard). The degree of substitution of the carbon atoms was determined by DEPT 135° experiments. Further assignments were made with the help of H,H and C,H COSY and C,H COLOC spectra. FT-IR and FT-Raman spectra were obtained using a Nicolet 320 FT-IR spectrometer and a Bruker FRA106 spectrometer, respectively. Mass spectra were recorded on a Finnigan MAT8430 spectrometer. UV/Vis absorption spectra were measured with a Hewlett Packard diode array spectrophotometer 8452A with 1 cm cuvettes. Solvents ("Uvasol", Merck) were used without further purification. Elemental analyses were carried out by the analytical laboratory of the Institute of Pharmaceutical Chemistry, Technical University of Braunschweig. Fluorescence spectra were run on a Perkin–Elmer luminescence spectrometer LS50B in non-degassed chloroform ("Uvasol"; $c = 10^{-5}$ mol L^{-1}). Fluorescence quantum yields were obtained by using commercially available standards. 1,4-Dioxane for EOA measurements was carefully purified and dried by column chromatography on basic alumina followed by distillation over sodium/potassium alloy under argon. The DFWM set-up was driven by an actively mode-locked quasi-cw Nd:YAG laser with a fiber/grating pulse compressor ($\lambda = 1064$ nm, $\tau_p \approx 5$–7 ps, with a repetition rate of 80 MHz and $\sim$15 nJ energy per pulse).

7-Methoxy-2,3,4,4a,5,6-hexahydronaphthalen-2-one (10a): *p*-Toluenesulfonic acid monohydrate (0.1 g, 0.53 mmol) was added to a stirred solution of **3** (2 g, 12.19 mmol) in toluene (200 mL) and anhydrous methanol (20 mL). After heating to reflux for 10 h with a Dean-Stark trap most of the methanol and water were removed by distillation. The mixture was washed with saturated $NaHCO_3$ solution (50 mL), brine (2×50 mL) and the organic layer was dried ($MgSO_4$). After evaporation of solvent and recrystallisation from *n*-pentane **10a** was obtained as a pale yellow solid (1.8 g, 83%, m.p. 94 °C; literature value 94–95 °C[19]).

7-*p*-Toluenesulfonyloxy-2,3,4,4a,5,6-hexahydronaphthalen-2-one (10b): *p*-Toluenesulfonyl chloride (1.02 g, 5.35 mmol) and **3** (0.8 g, 4.88 mmol) were suspended in anhydrous THF (20 mL) at 25 °C under a nitrogen atmosphere. After dropwise addition of triethylamine (0.84 mL, 6.03 mmol) over a period of about 2 min, the reaction mixture was stirred for 12 h at the same temperature. A clear yellow solution was obtained by filtration. Evaporation of solvent, flash chromatography (100 g SiO_2; toluene/$CHCl_3$/ethyl acetate 10:2:1, $R_f = 0.23$) afforded a viscous dark yellow oil that was transfered to an extraction thimble after dissolving in a few drops of CH_2Cl_2. Extraction with boiling *n*-pentane yielded a pale yellow solid (0.588 g, 38%, m.p. 92 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 7.81–7.83 (AA′ of AA′XX′, 2H; H-2′), 7.37–7.39 (XX′ of AA′XX′, 2H; H-3′), 5.91 (d, ^4J(H,H) = 2.4 Hz, 1H; H-1,8), 5.72 (s, 1H; H-1,8), 2.48 (s, 3H; CH_3), 2.31–2.53 (m, 5H), 2.05–2.12 (m, 1H), 1.92–1.98 (m, 1H), 1.63–1.80 (m, 1H), 1.45–1.56 (m, 1H; CH_2, CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 199.0$ (s, C-2), 156.4, 156.3 145.8, 132.8 (s, C-7,8a,1′,4′), 130.0, 128.2 (d, C-2′,3′), 125.4, 117.6 (d, C-1,8), 37.5 (t, C-3), 34.4 (d, C-4a), 29.9, 29.2, 28.8 (t, C-4,5,6), 21.7 (q, CH_3); FT-IR (KBr): $\tilde{\nu} = 1664$ (s, C=O), 1637 (vs), 1596 (s), 1364 (vs), 1193 (vs), 1180 (vs), 832 cm^{-1} (vs); UV/Vis ($CHCl_3$): λ_{max} (ε) = 282 nm (28300 dm^{3}mol^{-1}cm^{-1}); MS (70 eV, EI): *m*/*z* (%): 318 (41) $[M]^+$, 155 (100) $[SO_2 - C_6H_4 - CH_3]$; elemental analysis calcd (%) for $C_{17}H_{18}O_4S$ (318.4): C 64.13, H 5.70, S 10.07; found: C 64.19, H 5.71, S 10.15.

(2,3,4,4a,5,6-Hexahydro-7-*p*-toluenesulfonyloxy-2-naphthylidene)methanedicarbonitrile (11): Compound **10b** (0.49 g, 1.54 mmol) and malonitrile (0.2 g, 3.03 mmol) were dissolved in anhydrous DMF (5 mL). After addition of the catalyst (0.05 g piperidine and 0.03 g HOAc in DMF, 2 mL) the colour changed immediately from yellow to pink. The solution was stirred at 25 °C for 24 h and then the solvent was removed in vacuo. The residue was taken up in $CHCl_3$ (50 mL) and washed with water (2×30 mL with 3 mL of conc. HCl). Drying ($MgSO_4$), removal of solvent and flash chromatography (100 g SiO_2; toluene/$CHCl_3$/ethyl acetate 5:2:1, $R_f = 0.63$) gave **11** as a viscous yellow oil (0.173 g, ca. 25%) containing about 20% of toluene (^{1}H NMR analysis), which was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.75$–7.80 (AA′ of AA′XX′, 2H; H-2′), 7.35–7.39 (XX′ of AA′XX′, 2H; H-3′), 6.43 (s, 1H) and 6.02 (d,

0947-6539/02/0807-1584 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 7

^4J(H,H) = 1.9 Hz, 1H; H-1,8), 2.46 (s, 3H; CH_3), 2.95–3.06 (m, 1H), 2.26–2.77 (m, 4H), 1.89–2.09 (m, 2H), 1.28–1.73 (m, 2H; CH_2 and CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 169.1 (s, C-2), 158.7, 155.5, 146.0, 132.5 (s, C-7,8a,1′,4′), 130.0, 128.0 (d, C-2′,3′), 121.4, 117.1 (d, C-1,8), 113.1, 112.4 (s, C≡N), 77.7 (s, C-9), 34.5 (d, C-4a), 29.3 28.8, 28.8, 27.9 (t, C-3,4,5,6), 21.6 (q, CH_3).

7-Trifluormethanesulfonyloxy-2,3,4,4a,5,6,10,10a-octahydroanthracen-2-one (12b): Sodium hydride (suspension in oil, ca. 50%, 0.64 g, 13.33 mmol) was added in small portions to a suspension of **9** (2.75 g, 12.71 mmol) in anhydrous dimethoxyethane (100 mL) at 25 °C under a nitrogen atmosphere. The mixture was stirred for 12 h with a change of colour from yellow to dark orange. After cooling to −60 °C, a solution of *N*-phenylbistrifluoromethanesulfonimide (4.80 g, 13.44 mmol) in the same solvent (20 mL) was added dropwise within 30 min. After stirring at −60 °C for 1 h and warming to 25 °C within 12 h a clear brown solution was obtained. The solvent was removed and the residue was suspended in CH_2Cl_2. Filtration over SiO_2 (200 g) with CH_2Cl_2 as eluent (finally CH_2Cl_2/EtOH 20:1) afforded a viscous brown oil. Flash chromatography (200 g SiO_2; CH_2Cl_2/ethyl acetate 150:1, R_f = 0.17) furnished a brown oil, which solidified on standing to a yellow solid (2.66 g, 60%, m.p. 76–77 °C) and was used for synthetic purposes. An analytically pure sample (m.p. 77 °C) was obtained as pale yellow solid from *n*-hexane by slowly cooling down a stirred hot solution (without stirring **12b** precipitates as a green oil). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.24 (d, ^4J(H,H) = 2.5 Hz, 1H), 6.17 (s, 1H) and 5.84 (s, 1H; H-1,8,9), 2.38–2.75 (m, 6H), 2.00–2.15 (m, 3H), 1.68–1.79 (m, 1H; CH_2 and CH), 1.56 (dq, ^2J(H,H) = ^3J(H,H) = 13.1 Hz, ^3J(H,H) = 5.3 Hz, 1H; H_{ax}-4 or -5), 1.25 (q, ^2J(H,H) = ^3J(H,H) = 12.8 Hz, 1H; H_{ax}-10); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 199.7 (s, C-2), 157.4, 153.5, 143.9 (s, C-7,8a,9a), 127.9, 124.8, 119.7 (d, C-1,8,9), 118.4 (q, ^1J(C,F) = 320.6 Hz, CF_3), 37.8 (t, C-3), 36.1 (t, C-10), 35.5, 34.5 (d, C-4a,10a), 30.0, 29.3, 28.5 (t, C-4,5,6); FT-IR (KBr): $\tilde{\nu}$ = 1662 (s, C=O), 1636 (s), 1589 (vs), 1420 cm^{-1} (vs); UV/Vis ($CHCl_3$): λ_{max} (ε) = 318 nm (41000 dm^{3}mol^{-1}cm^{-1}); MS (70 eV, EI): *m*/*z* (%): 348 (50) $[M]^+$, 215 (51), 187 (100); elemental analysis calcd (%) for $C_{15}H_{15}F_3O_4S$ (348.3): C 51.72, H 4.34, S 9.21; found: C 51.70, H 4.17, S 9.27.

(2,3,4,4a,5,6,10,10a-Octahydro-7-hydroxy-2-anthrylidene)methanedicarbonitrile (13): The reaction of **9** (0.5 g, 2.31 mmol) and malonitrile (0.183 g, 2.77 mmol) was carried out as described for **11** in DMF (10 mL) and with the catalyst (0.250 g piperidine and 0.15 g HOAc in DMF, 5 mL). The solvent was removed in vacuo, and the residue was taken up in $CHCl_3$ (50 mL) and washed with water (150 mL, with a few drops of conc. HCl). After extraction of the aequous phase with $CHCl_3$ (3 × 20 mL) the combined organic solutions were again washed with acidified water (vide supra, 3 × 100 mL) and water (3 × 100 mL). Drying of the dark red solution ($MgSO_4$), removal of solvent and filtration over silicagel (6 cm layer, 50 g SiO_2; $CHCl_3$/EtOH 40:1) afforded a dark solid with metallic lustre (0.333 g, ca. 54%) that was used for synthetic purposes. An analytical sample was obtained by flash chromatography (50 g SiO_2; $CHCl_3$/EtOH 40:1, R_f = 0.38) starting from 0.13 g of the crude product and recrystallisation from methanol as thin red needles (0.024 g, ca. 20%, m.p. 215–217 °C (part. decomp)). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 10.65 (br s, 1H; OH), 6.25 (s, 1H), 6.01 (s, 1H) and 5.57 (s, 1H; H-1,8,9), 2.76–2.79 (m, 1H), 2.42–2.66 (m, 4H), 2.19–2.24 (m, 1H), 1.87–1.97 (m, 3H), 1.32–1.45 (m, 2H; CH_2 and CH), 1.12 (q, ^2J(H,H) = ^3J(H,H) = 12.4 Hz, 1H; H_{ax}-10); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 170.0 (s, C-2), 168.8, 162.2, 158.9 (s, C-7,8a,9a), 115.4, 114.7 (s, C≡N), 117.9, 114.9, 103.0 (d, C-1,8,9), 67.2 (s, C-11), 35.6, 35.1 (d, C-4a,10a), 35.9, 29.0, 29.0, 28.8, 28.3 (t, C-3,4,5,6,10); FT-IR (KBr): $\tilde{\nu}$ = 3213 (w, O–H), 2227, 2207 (s, C≡N), 1607 (s), 1537 (vs), 1533 (vs), 1530 (vs), 1491 (vs), 1335 (s), 1170 (vs), 887 cm^{-1} (s); UV/Vis ($CHCl_3$): λ_{max} (ε) = 458 nm (49600 dm^{3}mol^{-1}cm^{-1}); MS (70 eV, EI): *m*/*z* (%): 264 (100) $[M]^+$; elemental analysis calcd (%) for $C_{17}H_{16}N_2O$ (264.3): C 77.25, H 6.10, N 10.60; found: C 77.22, H 6.01, N 10.50.

(2,3,4,4a,5,6,10,10a-Octahydro-7-*p*-toluenesulfonyloxy-2-anthrylidene)-methanedicarbonitrile (14): A suspension of **13** (1 g, ca. 3.78 mmol) and *p*-toluenesulfonyl chloride (0.865 g, 4.54 mmol) in anhydrous $CHCl_3$ (20 mL) was cooled to 0 °C and anhydrous pyridine (1 mL, 12.40 mmol) was added dropwise over a period of 2 min. After warming up to 25 °C over a period of 12 h, the mixture was poured onto crushed ice (ca. 20 mL) and conc. HCl (1 mL). $CHCl_3$ (30 mL) was added and the separated organic layer was washed with brine (3 × 20 mL) and dried ($MgSO_4$). After evaporation of solvent and flash chromatography (100 g SiO_2; toluene/$CHCl_3$/ethyl acetate 20:4:1, R_f = 0.37) the viscous oil was transferred to an extraction thimble and extracted with boiling diethyl ether. Compound **14** was obtained as a yellow solid (0.603 g, 38%, m.p. 158 °C). Material of sufficient purity for synthetic purposes can be obtained by filtration of the crude product over SiO_2 (ca. 20 g; $CHCl_3$/EtOH 40:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.80–7.83 (AA′ of AA′XX′, 2H; H-2′), 7.37–7.39 (XX′ of AA′XX′, 2H; H-3′), 6.52 (s, 1H), 6.01 (s, 1H) and 5.91 (d, ^4J(H,H) = 2.2 Hz, 1H; H-1,8,9), 2.49 (s, 3H; CH_3), 3.01–3.07 (m, 1H), 2.31–2.58 (m, 5H), 2.02–2.08 (m, 1H), 1.90–1.99 (m, 2H) and 1.39–1.52 (m, 2H; CH_2 and CH), 1.19 (q, ^2J(H,H) = ^3J(H,H) = 12.4 Hz, 1H; H_{ax}-10); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 169.5 (s, C-2), 157.3, 155.2, 149.0, 145.7, 133.0 (s, C-7,8a,9a,1′,4′), 129.0 and 128.2 (d, C-2′,3′), 125.9, 120.7, 118.3 (d, C-1,8,9), 113.7, 113.0 (s, C≡N), 76.4 (s, C-11), 35.9, 34.8 (d, C-4a,10a), 36.0, 29.5, 29.4, 28.8, 28.6 (t, C-3,4,5,6,10), 21.8 (q, CH_3); FT-IR (KBr): $\tilde{\nu}$ = 2218, 2210 (s, C≡N), 1554 (vs), 1514 (vs), 1367 (s), 1199 (s), 1080 (s), 846 cm^{-1} (s); UV/Vis ($CHCl_3$): λ_{max} (ε) = 404 nm (49500 dm^{3}mol^{-1}cm^{-1}); MS (70 eV, EI): *m*/*z* (%): 418 (94) $[M]^+$, 263 (100); elemental analysis calcd (%) for $C_{24}H_{22}N_2O_3S$ (418.5): C 68.88, H 5.30, N 6.69, S 7.66; found: C 68.68, H 5.08, N 6.42, S 7.68.

7-(4-*N*,*N*-Di-*n*-butylaminophenyl)-2,3,4,4a,5,6-hexahydronaphthalen-2-one (15a): *p*-Bromo-*N*,*N*-di-*n*-butylaniline[53] (1.31 g, 4.61 mmol) was added dropwise over a period of about 5 min to a solution of *n*-BuLi (15% in *n*-hexane, 3.20 mL, 5.10 mmol) and *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine (TMEDA, 0.77 mL, 5.10 mmol) in anhydrous diethyl ether (20 mL) at 25 °C. After heating to reflux for 30 min, the bright yellow solution was cooled to −80 °C and a small amount of precipitate was formed. A solution of **10a** (0.750 g, 4.21 mmol) in anhydrous diethyl ether (20 mL) was added over a period of 30 min at that temperature, and the reaction was allowed to reach 25 °C over 12 h. After quenching with saturated NH_4Cl solution (10 mL), HCl (2 N) was added to the mixture until an acidic reaction was observed. The phases were separated and the aqueous phase was extracted with diethyl ether (2 × 50 mL). The combined organic phases were washed with water (50 mL) and dried ($MgSO_4$), and the solvent was removed. Flash chromatography (100 g SiO_2; toluene/$CHCl_3$/ethyl acetate 10:2:1, R_f = 0.27) and extraction with boiling *n*-pentane afforded **15a** as bright yellow microcrystals (0.23 g, 16%, m.p. 92–94 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.43–7.45 (AA′ of AA′XX′, 2H; H-2′), 6.60–6.62 (XX′ of AA′XX′, 2H; H-3′), 6.57 (d, ^4J(H,H) = 1.9 Hz, 1H; H-8), 5.84 (s, 1H; H-1), 3.30 (t, ^3J(H,H) = 7.7 Hz, 4H; H-1″), 2.79–2.84 (m, 1H; H_{eq}-6), 2.38–2.64 (m, 4H; H-3,4a, H_{ax}-6), 2.05–2.12 (m, 2H; H_{eq}-4,5), 1.68–1.79 (m, 1H; H_{ax}-4), 1.47–1.61 (m, 5H; H-2″, H_{ax}-5), 1.31–1.40 (m, 4H; H-3″), 0.96 (t, ^3J(H,H) = 7.3 Hz, 6H; H-4″); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 8; further signals: δ = 148.7 (s, C-4′), 126.9 (d, C-2′), 125.5 (s, C-1′), 111.2 (d, C-3′), 50.7 (t, C-1″), 37.9 (t, C-3), 35.5 (d, C-4a), 30.2 (t, C-4), 29.8 (t, C-5), 29.4 (t, C-2″), 27.8 (t, C-6), 20.3 (t, C-3″), 14.0 (q, C-4″); FT-IR (KBr): $\tilde{\nu}$ = 1682 (vs, C=O), 1620 (vs), 1535 (s), 1486 (m), 1436 (m), 1239 (m), 1089 cm^{-1} (m); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 351 (85) $[M]^+$ 308 (100); elemental analysis calcd (%) for $C_{24}H_{33}NO$ (351.5): C 82.00, H 9.46, N 3.98; found: C 81.93, H 9.49, N 3.80.

7-(5-Piperidino-2-thienyl)-2,3,4,4a,5,6-hexahydronaphthalen-2-one (15b): The lithium salt of 2-piperidinothiophene[54] (0.619 g, 3.70 mmol) was prepared as described in the previous experiment using *n*-Buli (15% in *n*-hexane, 2.52 mL, 4.07 mmol) and TMEDA (0.56 mL, 3.71 mmol) in diethyl ether (20 mL). Cooling to −80 °C afforded a cream suspension. During the addition of a solution of **10a** (0.6 g, 3.37 mmol) in anhydrous diethyl ether (15 mL) at the given temperature, the mixture turned red and after warming up to 25 °C within 12 h a clear yellow solution was obtained. The reaction was quenched with saturated NH_4Cl solution (5 mL) and water (20 mL) was added. The resulting green solution was extracted with diethyl ether (3 × 30 mL). Acidification of the aqueous layer with 2 N HCl (5 mL) and extraction with $CHCl_3$ (3 × 30 mL) afforded a bright yellow solution that was combined with the residue from the above-mentioned ethereal extract. The combined organic layers were washed with 0.2 N HCl (100 mL) and brine (100 mL) and dried ($MgSO_4$), and the solvent was removed. Flash chromatography (100 g SiO_2; toluene/$CHCl_3$/ethyl acetate 5:2:1, R_f = 0.32) and extraction with boiling diethyl ether furnished **15b** as dark yellow powder (0.387 g, 37%, m.p. 148 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.97 (d, ^3J(H,H) = 4.2 Hz, 1H; H-3′), 6.27 (d, ^4J(H,H) = 1.4 Hz, 1H; H-8), 5.95 (d, ^3J(H,H) = 4.2 Hz, 1H; H-4′), 5.78 (s, 1H; H-1), 3.21 (t, ^3J(H,H) = 5.5 Hz, 4H; H-2″), 2.77–2.82 (m, 1H; H_{eq}-6), 2.37–2.57 (m, 4H;

H-3,4a, H_{ax}-6), 2.00–2.10 (m, 2H; H_{eq}-4,5), 1.45–1.77 (m, 8H; H_{ax}-4,5, H-3″,4″); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 8; further signals: $\delta = 161.3$ (s, C-5′), 127.9 (s, C-2′), 127.1 (d, C-3′), 103.9 (d, C-4′), 51.4 (t, C-2″), 37.8 (t, C-3), 35.5 (d, C-4a), 30.2 (t, C-4), 29.3 (t, C-5), 27.3 (t, C-6), 25.0 (t, C-3″), 23.6 (t, C-4″); FT-IR (KBr): $\tilde{\nu} = 1683$ (vs, C=O), 1599 (vs), 1504 (vs), 1462 (s), 1286 (m), 1219 (m), 1044 cm^{-1} (m); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 813 (100) $[M]^+$, 285 (24); elemental analysis calcd (%) for $C_{19}H_{23}NOS$ (313.5): C 72.80, H 7.40, N 4.47, S 10.23; found: C 72.71, H 7.49, N 4.27, S 10.09.

[2,3,4,4a,5,6-Hexahydro-7-(4-*N*,*N*-di-*n*-butylaminophenyl)-2-naphthylidene]methanedicarbonitrile (16a): A solution of **15a** (0.4 g, 1.14 mmol) in anhydrous CH_2Cl_2 (30 mL) was cooled to 0 °C and trimethyloxonium tetrafluoroborate (0.207 g, 1.40 mmol) was added rapidly in small portions with the colour of the solution changing immediately from bright yellow to dark red. The mixture was allowed to reach 25 °C over 12 h. Diethyl ether (200 mL) was added dropwise to the stirred solution, the resulting precipitate (0.358 g) was isolated by vacuum filtration as dark blue solid and was used without further purification. To a solution of the latter in anhydrous pyridine (5 mL), malonitrile (0.153 g, 2.32 mmol) was added and a change in colour was observed from yellow to red. The mixture was heated to 80 °C and further malonitrile (3 × 0.05 g, 2.27 mmol) was added over a period of about 3 h. After cooling to 25 °C $CHCl_3$ (50 mL) and HCl (2N, 50 mL) were added. After phase separation the aqueous layer was extracted with $CHCl_3$ (3 × 10 mL), the combined organic layers were washed with HCl (2N, 50 mL) and brine (2 × 50 mL) and dried ($MgSO_4$), and the solvent was removed. Flash chromatography (100 g SiO_2; $CHCl_3$/*n*-hexane 5:3, $R_f = 0.46$) and extraction with boiling *n*-pentane afforded a dark blue solid (0.16 g, 35%, m.p. 123–124 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.47$–7.49 (AA′ of AA′XX′, 2H; H-2′), 6.69 (d, ^4J(H,H) = 1.4 Hz, 1H; H-8), 6.61–6.64 (XX′ of AA′XX′, 2H; H-3′), 6.57 (s, 1H; H-1), 3.32 (t, ^3J(H,H) = 7.7 Hz, 4H; H-1″), 3.01–3.05 (m, 1H; H_{eq}-3), 2.88–2.93 (m, 1H; H_{eq}-6), 2.43–2.67 (m, 3H; H_{ax}-3,6, H-4a), 2.05–2.09 (m, 2H; $H_{ax/eq}$-4,5), 1.44–1.63 (m, 6H; $H_{ax/eq}$-4,5, H-2″), 1.32–1.42 (m, 4H; H-3″), 0.97 (t, ^3J(H,H) = 7.3 Hz, 6H; H-4″); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 8; further signals: $\delta = 149.4$ (s, C-4′), 127.4 (d, C-2′), 124.7 (s, C-1′), 114.7, 114.0 (s, C≡N), 111.3 (d, C-3′), 50.7 (t, C-1″), 35.8 (C-4a), 29.6 (2t, C-3,5), 29.4 (t, C-2″), 28.8 (t, C-4), 27.7 (t, C-6), 20.3 (t, C-3″), 14.0 (q, C-4″); FT-IR (KBr): $\tilde{\nu} = 2213$ (m, C≡N), 1607 (m), 1547 (vs), 1501 (vs), 1361 (m), 1200 cm^{-1} (vs); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 399 (89) $[M]^+$, 356 (100), 314 (58); elemental analysis calcd (%) for $C_{27}H_{33}N_3$ (399.6): C 81.16, H 8.32, N 10.52; found: C 81.00, H 8.42, N 10.52.

[2,3,4,4a,5,6-Hexahydro-7-(5-piperidino-2-thienyl)-2-naphthylidene]methanedicarbonitrile (16b): As described in the previous experiment **15b** (0.4 g, 1.28 mmol) was treated with trimethyloxonium tetrafluoroborate (0.227 g, 1.54 mmol) in CH_2Cl_2 (30 mL). Precipitation with diethyl ether (200 mL) afforded a dark solid (0.443 g) that was used without purification. This intermediate (0.32 g) and malonitrile (0.153 g, 2.32 mmol) were heated in anydrous pyridine (5 mL) to 80 °C, kept at this temperature for 15 min and then cooled to 25 °C. Aqueous workup (vide supra), flash chromatography (50 g SiO_2; $CHCl_3$, $R_f = 0.14$) and extraction with boiling diethyl ether gave **16b** as a dark grey-green solid (0.106 g, ca. 32%, m.p. 237 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.09$ (d, ^3J(H,H) = 4.2 Hz, 1H; H-3′), 6.47 (s, 1H; H-1), 6.33 (s, 1H; H-8), 6.01 (d, ^3J(H,H) = 4.2 Hz, 1H; H-4′), 3.29 (t, ^3J(H,H) = 5.4 Hz, 4H; H-2″), 2.96–3.12 (m, 1H; H_{eq}-3), 2.84–2.89 (m, 1H; H_{eq}-6), 2.39–2.72 (m, 3H; H_{ax}-3,6, H-4a), 2.01–2.17 (m, 2H; H_{eq}-4,5), 1.63–1.89 (m, 6H; H-3″,4″), 1.41–1.55 (m, 2H; H_{ax}-4,5); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 8; further signals: $\delta = 163.0$ (s, C-5′), 129.7 (d, C-3′), 127.2 (s, C-2′), 115.1, 114.4 (s, C≡N), 104.6 (d, C-4′), 51.3 (t, C-2″), 35.9 (d, C-4a), 29.5 (t, C-3), 29.2 (t, C-5), 28.8 (t, C-4), 27.4 (t, C-6), 25.0 (t, C-3″), 23.6 (t, C-4″); FT-IR (KBr): $\tilde{\nu} = 2203$ (s, C≡N), 1541 (m), 1437 (vs), 1433 (vs), 1395 (s), 1337 (vs), 1307 (s), 1200 (vs), 1182 (vs), 1089 (vs), 1080 cm^{-1} (vs); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 361 (100) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{23}N_3S$ (361.5): C 73.09, H 6.41, N 11.62, S 8.87; found: C 72.97, H 6.35, N 11.54, S 8.77.

(2,3,4,4a,5,6-Hexahydro-7-piperidino-2-naphthylidene)methanedicarbonitrile (17): Anhydrous piperidine (0.051 mL, 0.52 mmol) and sodium hydride (suspension in oil, ca. 50%, 0.021 g, ca. 0.52 mmol) were added to a solution of **11** (0.16 g, ca. 0.35 mmol) in anhydrous CH_3CN (10 mL), and the mixture was heated to reflux for 14 h. After cooling, filtration and evaporation of solvent, the residue was purified by flash chromatography (50 g, SiO_2; toluene/$CHCl_3$/ethyl acetate 5:2:1, $R_f = 0.31$) and extraction with boiling diethyl ether. Compound **17** formed as thin red needles (0.089 g, ca. 91%, m.p. 183 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.19$ (s, 1H; H-1), 5.55 (s, 1H; H-8), 3.41–3.51 (m, 4H; H-2′), 2.89 (ddd, ^2J(H,H) = 17.4 Hz, ^3J(H,H) = 4.1, 2.2 Hz, 1H; H_{eq}-3), 2.64 (ddd, ^2J(H,H) = 16.8 Hz, ^3J(H,H) = 4.7, 2.0 Hz, 1H; H_{eq}-6), 2.29–2.50 (m, 3H; H_{ax}-3,6, H-4a), 1.95–2.17 (m, 2H; H_{eq}-4,5), 1.58–1.90 (m, 6H; H-3′,4′), 1.19–1.56 (m, 2H; H_{ax}-4,5); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 8; further signals: $\delta = 117.5$, 116.7 (s, C≡N), 48.1 (t, C-2′), 35.2 (d, C-4a), 29.3 (t, C-3), 29.2 (t, C-5), 28.8 (t, C-4), 27.7 (t, C-6), 25.9 (t, C-3′), 24.2 (t, C-4′); FT-IR (KBr): $\tilde{\nu} = 2195$, 2183 (vs, C≡N), 1523 (vs), 1480 (vs), 1449 (vs), 1379 (s), 1204 cm^{-1} (vs); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 279 (100) $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{21}N_3$ (279.4): C 77.38, H 7.58, N 15.04; found: C 77.47, H 7.72, N 14.98.

7-(4-*n*-Butylphenyl)-2,3,4,4a,5,6,10,10a-octahydroanthracen-2-one (18a): *t*Buli (15% in *n*-pentane, 4.20 mL, 6.49 mmol) was added dropwise to a solution of *p*-bromo-*n*-butylbenzene (0.57 mL, 3.23 mmol) in anhydrous THF (50 mL) at −78 °C. After stirring for 1 h a solution of **12a** (0.68 g, 2.95 mmol) in THF (20 mL) was added over 40 min at the same temperature. The mixture was allowed to reach 25 °C over a period of 12 h and was quenched by addition of saturated NH_4Cl solution (20 mL). The solvent was removed, and the residue was taken up in $CHCl_3$ (50 mL), shaken with acetic acid (20% in water, 50 mL), washed with water (2 × 50 mL) and dried ($MgSO_4$). After flash chromatography (100 g SiO_2; toluene/$CHCl_3$/ethyl acetate 10:2:1, $R_f = 0.16$) and extraction with boiling *n*-pentane a bright yellow solid was obtained (0.532 g, 54%, m.p. 152 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.40$–7.42 (AA′ of AA′XX′, 2H; H-2′), 7.16–7.18 (XX′ of AA′XX′, 2H; H-3′), 6.63 (d, ^4J(H,H) = 2.0 Hz, 1H; H-8), 6.12 (s, 1H; H-9), 5.82 (s, 1H; H-1), 2.70–2.76 (m, 1H; H_{eq}-6), 2.61 (t, ^3J(H,H) = 7.7 Hz, 2H; H-1″), 2.37–2.66 (m, 5H; H-3,4a,10a, H_{ax}-6), 1.97–2.12 (m, 3H; H_{eq}-4,5,10), 1.68–1.79 (m, 1H; H_{ax}-4), 1.56–1.64 (m, 2H; H-2″), 1.48 (dq, ^2J(H,H) = ^3J(H,H) = 12.6 Hz, ^3J(H,H) = 5.1 Hz, 1H; H_{ax}-5), 1.33–1.40 (m, 2H; H-3″), 1.27 (q, ^2J(H,H) = ^3J(H,H) = 12.3 Hz, 1H; H_{ax}-10), 0.93 (t, ^3J(H,H) = 7.4 Hz, 3H; H-4″); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 5; further signals: $\delta = 143.3$ (s, C-4′), 137.5 (s, C-1′), 128.6 (d, C-3′), 125.2 (C-2′), 37.9 (t, C-3), 36.9 (t, C-10), 36.0 (d, C-4a), 35.8 (d, C-10a), 35.3 (t, C-1″), 33.5 (t, C-2″), 30.3 (t, C-4), 30.0 (t, C-5), 28.0 (t, C-6), 22.3 (t, C-3″), 13.9 (q, C-4″); FT-IR (KBr): $\tilde{\nu} = 1650$ (vs, C=O), 1578 (vs), 1201 (m), 1170 (m), 907 cm^{-1} (m); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 332 (100) $[M]^+$, 304 (28); elemental analysis calcd (%) for $C_{24}H_{28}O$ (332.5): C 86.70, H 8.49; found: C 86.68, H 8.63.

7-(5-*n*-Butyl-2-thienyl)-2,3,4,4a,5,6,10,10a-octahydroanthracen-2-one (18b): 2-*n*-Butylthiophene (0.336 g, 2.40 mmol) was converted into its lithium salt as described for **15a** by using *n*-Buli (15% in *n*-hexane, 1.65 mL, 2.64 mmol) and TMEDA (0.36 mL, 2.39 mmol) in anhydrous diethyl ether (10 mL). After cooling to −80 °C, a solution of **12a** (0.500 g, 2.17 mmol) in anhydrous THF (20 mL) was added over 20 min. The mixture was stirred at this temperature for 1 h and was then allowed to reach 25 °C over a period of 12 h. The reaction was quenched with saturated NH_4Cl solution (5 mL), and the aqueous phase was extracted with diethyl ether (3 × 30 mL). After evaporation of solvent the residue was taken up in $CHCl_3$ (50 mL), shaken with 2N HCl (50 mL), neutralised, washed with saturated $NaHCO_3$ solution (50 mL) and water (2 × 50 mL), and dried ($MgSO_4$). Purification by flash chromatography (100 g SiO_2; toluene/$CHCl_3$/ethyl acetate 5:2:1, $R_f = 0.45$) and extraction with boiling *n*-pentane yielded **18b** as yellow solid (0.147 g, 20%, m.p. 101 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.96$ (d, ^3J(H,H) = 3.6 Hz, 1H; H-3′), 6.69 (d, ^3J(H,H) = 3.6 Hz, 1H; H-4′), 6.51 (d, ^4J(H,H) = 1.8 Hz, 1H; H-8), 6.08 (s, 1H; H-9), 5.80 (s, 1H; H-1), 2.71–2.80 (m, 3H; H_{eq}-6, H-1″), 2.34–2.57 (m, 5H; H-3,4a,10a, H_{ax}-6), 1.94–2.00 (m, 3H; H_{eq}-4,5,10), 1.61–1.77 (m, 3H; H_{ax}-4, H-2″), 1.34–1.51 (m, 3H; H_{ax}-5, H-3″), 1.24 (q, ^2J(H,H) = ^3J(H,H) = 12.4 Hz, 1H; H_{ax}-10), 0.93 (t, ^3J(H,H) = 7.3 Hz, 3H; H-4″); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 5; further signals: $\delta = 146.9$ (s, C-5′), 142.3 (s, C-2′), 125.0 (d, C-4′), 124.2 (d, C-3′), 37.9 (t, C-3), 36.9 (t, C-10), 35.9 (d, C-4a), 35.7 (d, C-10a), 33.6 (t, C-2″), 30.2 (C-4), 30.0 (t, C-1″), 29.5 (t, C-5), 27.7 (t, C-6), 22.1 (t, C-3″), 13.8 (q, C-4″); FT-IR (KBr): $\tilde{\nu} = 1646$ (vs, C=O), 1575 (vs), 1561 (s), 1383 (m), 1253 (m), 1198 cm^{-1} (m); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 338 (100) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{26}OS$ (338.5): C 78.06, H 7.74, S 9.47; found: C 77.93, H 7.83, S 9.50.

7-(4-*N*,*N*-Dimethylaminophenyl)-2,3,4,4a,5,6,10,10a-octahydroanthracen-2-one (18c): *p*-Bromo-*N*,*N*-dimethylaniline (0.71 g, 3.55 mmol) in anhy-

0947-6539/02/0807-1586 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 7

drous diethyl ether (15 mL) was added to *n*-Buli (15% in *n*-hexane, 2.67 mL, 4.26 mmol) and TMEDA (0.64 mL, 4.24 mmol) over 10 min at such a rate that the temperature did not rise above 20 °C. The solution was stirred for 45 min and then added by a syringe to a suspension of **12a** (0.400 g, 1.74 mmol) in anhydrous THF (20 mL) at −40 °C within 40 min. After stirring at this temperature for 1 h and warming up to 25 °C over 15 h, the reaction was quenched by the addition of saturated NH_4Cl solution (15 mL). The resulting suspension was extracted with $CHCl_3$ (3 × 50 mL), the combined organic phases were dried ($MgSO_4$) and the solvent was removed. Flash chromatography (150 g SiO_2; toluene/$CHCl_3$/ethyl acetate 3:3:1, $R_f = 0.30$) and recrystallisation from toluene with a few drops of $CHCl_3$ afforded **18c** as thin red needles (0.278 g, 50%, m.p. 267 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.42-7.45$ (AA′ of AA′XX′, 2H; H-2′), 6.68–6.72 (XX′ of AA′XX′, 2H; H-3′), 6.58 (d, $^4J(H,H) = 2.1$ Hz, 1H; H-8), 6.09 (s, 1H; H-9), 5.80 (s, 1H; H-1), 2.99 (s, 6H; CH_3), 2.77 (ddd, $^2J(H,H) = 17.6$ Hz, $^3J(H,H) = 4.9$, 2.2 Hz, 1H; H_{eq}-6), 2.38–2.60 (m, 5H; H-3,4a,10a, H_{ax}-6), 1.97–2.12 (m, 3H; H_{eq}-4,5,10), 1.69–1.80 (m, 1H; H_{ax}-4), 1.43–1.54 (dq, $^2J(H,H) = 12.8$ Hz, $^3J(H,H) = 4.9$ Hz, 1H; H_{ax}-5), 1.28 (q, $^2J(H,H) = {}^3J(H,H) = 12.4$ Hz, 1H; H_{ax}-10); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 5; further signals: $\delta = 150.5$ (s, C-4′), 127.7 (s, C-1′), 126.3 (d, C-2′), 112.1 (d, C-3′), 40.3 (q, CH_3), 38.0 (t, C-3), 37.1 (t, C-10), 36.1, 35.9 (d, C-4a,10a), 30.4 (t, C-4), 30.1 (t, C-5), 27.7 (t, C-6); FT-IR (KBr): $\tilde{\nu} = 1653$ (s, C=O), 1612 (s), 1567 (vs), 1542 (s), 1525 (s), 1446 (m), 1374 (s), 1256 (m), 1170 cm^{-1} (s); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 319 (100) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{25}NO$ (319.5): C 82.72, H 7.89, N 4.39; found: C 82.81, H 8.00, N 4.24.

7-(4-*N*,*N*-Di-*n*-butylaminophenyl)-2,3,4,4a,5,6,10,10a-octahydroanthracen-2-one (18d): *n*-Buli (15% in *n*-hexane, 3.60 mL, 5.8 mmol) was added dropwise to a solution of *p*-bromo-*N*,*N*-di-*n*-butylaniline[53] (1.5 g, 5.28 mmol) in anhydrous THF (20 mL) at −78 °C within 5 min. The mixture was stirred at this temperature for 2 h. After addition of a solution of **12a** (1.10 g, 4.78 mmol) in anhydrous THF (10 mL) at −78 °C over 30 min, the white suspension turned to an orange solution that was allowed to reach 25 °C over a period of 12 h. Saturated NH_4Cl solution (50 mL) was added, and the mixture was stirred for 15 min. Phase separation after addition of diethyl ether (50 mL), extraction of the aqueous layer with the same solvent (2 × 50 mL) and drying ($MgSO_4$) was followed by repeated flash chromatography (2 × 200 g SiO_2; toluene/$CHCl_3$/ethyl acetate 5:2:1, $R_f = 0.38$). Compound **18d** was finally obtained by extraction with boiling diethyl ether as yellow solid (0.653 g, 31%, m.p. 157–159 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.39-7.41$ (AA′ of AA′XX′, 2H; H-2′), 6.56–6.62 (XX′ of AA′XX′, 2H; H-3′), 6.55 (s, 1H; H-8), 6.06 (s, 1H; H-9), 5.79 (s, 1H; H-1), 3.29 (t, $^3J(H,H) = 7.6$ Hz, 4H; H-1″), 2.75 (ddd, $^2J(H,H) = 17.6$ Hz, $^3J(H,H) = 4.8$, 2.0 Hz, 1H; H_{eq}-6), 2.35–2.58 (m, 5H; H-3,4a,10a, H_{ax}-6), 1.94–2.09 (m, 3H; H_{eq}-4,5,10), 1.66–1.77 (m, 1H; H_{ax}-4), 1.53–1.61 (m, 4H; H-2″), 1.45 (dq, $^2J(H,H) = 12.7$ Hz, $^3J(H,H) = 4.9$ Hz, 1H; H_{ax}-5), 1.30–1.38 (m, 4H; H-3″), 1.25 (q, $^2J(H,H) = {}^3J(H,H) = 12.5$ Hz, 1H; H_{ax}-10), 0.96 (t, $^3J(H,H) = 7.3$ Hz, 6H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 5; further signals: $\delta = 148.2$ (s, C-4′), 126.5 (d, C-2′), 126.2 (s, C-1′), 111.2 (d, C-3′), 50.7 (t, C-1″), 37.9 (t, C-3), 37.0 (t, C-10), 36.0 (d, C-4a), 35.9 (d, C-10a), 30.3 (t, C-4), 30.1 (t, C-5), 29.4 (t, C-2″), 27.6 (t, C-6), 20.3 (t, C-3″), 14.0 (q, C-4″); FT-IR (KBr): $\tilde{\nu} = 1649$ (vs, C=O), 1609 (s), 1568 (vs), 1520 (vs), 1371 (s), 1201 (s), 898 cm^{-1} (s); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 403 (100) $[M]^+$, 360 (38); elemental analysis calcd (%) for $C_{28}H_{37}NO$ (403.6): C 83.33, H 9.24, N 3.47; found: C 83.35, H 9.26, N 3.21.

7-(5-Piperidino-2-thienyl)-2,3,4,4a,5,6,10,10a-octahydroanthracen-2-one (18e): A suspension of the lithium salt [prepared by adding neat 2-piperidinothiophene[54](1.45 g, 8.67 mmol) dropwise to TMEDA (1.70 mL, 11.26 mmol) and *n*-Buli (15% in *n*-hexane, 6.50 mL, 10.40 mmol) in anhydrous diethyl ether (10 mL) at 25 °C within 5 min and additional stirring for 1 h] was added by a syringe to a solution of **12a** (1.00 g, 4.34 mmol) in anhydrous THF (40 mL) at −40 °C. By following the procedure described for **18c** (using 30 mL NH_4Cl-solution), flash chromatography (200 g SiO_2; toluene/$CHCl_3$/ethyl acetate 3:3:1, $R_f = 0.32$) and extraction with boiling MeOH, **18e** was obtained as dark red solid (0.221 g, 14%, m.p. 226 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.88$ (d, $^3J(H,H) = 4.1$ Hz, 1H; H-3′), 6.30 (s, 1H; H-8), 6.02 (s, 1H; H-9), 5.94 (d, $^3J(H,H) = 4.1$ Hz, 1H; H-4′), 5.77 (s, 1H; H-1), 3.19 (t, $^3J(H,H) = 5.6$ Hz, 4H; H-2″), 2.73 (ddd, $^2J(H,H) = 17.4$ Hz, $^3J(H,H) = 4.8$, 2.1 Hz, 1H; H_{eq}-6), 2.36–2.61 (m, 5H; H-3,4a,10a, H_{ax}-6), 2.04–2.10 (m, 1H; H_{eq}-4), 1.93–2.00 (m, 2H; H_{eq}-5,10), 1.67–1.78 (m, 5H; H_{ax}-4, H-3″), 1.56–1.61 (m, 2H; H-4″), 1.45 (dq, $^2J(H,H) = {}^3J(H,H) = 12.8$ Hz, $^3J(H,H) = 4.8$ Hz, 1H; H_{ax}-5), 1.26 (q, $^2J(H,H) = {}^3J(H,H) = 12.4$ Hz, 1H; H_{ax}-10); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 5; further signals: $\delta = 160.3$ (s, C-5′), 129.2 (s, C-2′), 125.6 (d, C-3′), 104.1 (d, C-4′), 51.6 (t, C-2″), 37.9 (t, C-3), 37.0 (t, C-10), 36.1 (d, C-4a), 35.9 (d, C-10a), 30.4 (t, C-4), 29.6 (t, C-5), 27.1 (t, C-6), 25.1 (t, C-3″), 23.7 (t, C-4″); FT-IR (KBr): $\tilde{\nu} = 1639$ (s, C=O), 1582 (vs), 1562 (vs), 1475 (vs), 1443 (vs), 1378 cm^{-1} (vs); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 365 (100) $[M]^+$; elemental analysis calcd (%) for $C_{23}H_{27}NOS$ (365.5): C 75.57, H 7.44, N 3.83, S 8.77; found: C 75.54, H 7.55, N 3.71, S 8.65.

[2,3,4,4a,5,6,10,10a-Octahydro-7-(4-*n*-butylphenyl)-2-anthrylidene]methanedicarbonitrile (19a): Malonitrile (0.05 g, 0.76 mmol) and the catalyst (0.05 g piperidine and 0.03 g HOAc in DMF, 2 mL) were added to a solution of **18a** (0.2 g, 0.6 mmol) in anhydrous DMF (8 mL), and the mixture was heated to 80 °C under a nitrogen atmosphere. After 4 h, further malonitrile was added (0.02 g, 0.3 mmol) and stirring was continued for 17 h. After cooling, the solvent was removed in vacuo and the residue was taken up in $CHCl_3$ (50 mL). Washing with water with a few drops of conc. HCl (30 mL,) and water (2 × 50 mL), and drying ($MgSO_4$) was followed by repeated flash chromatography (1. 50 g SiO_2; $CHCl_3$/cyclohexane 1:1, $R_f = 0.28$, 2. 50 g SiO_2; $CHCl_3$). Compound **19a** was obtained as a hemihydrate by recrystallisation from cyclohexane as orange tablets (0.144 g; 63%, m.p. 129 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.42-7.45$ (AA′ of AA′XX′, 2H; H-2′), 7.18–7.20 (XX′ of AA′XX′, 2H; H-3′), 6.68 (d, $^4J(H,H) = 2.0$ Hz, 1H; H-8), 6.56 (s, 1H; H-1), 6.19 (s, 1H; H-9), 3.00–3.06 (m, 1H; H_{eq}-3), 2.76–2.81 (m, 1H; H_{eq}-6), 2.49–2.70 (m, 6H; H_{ax}-3,6, H-4a,10a,1″), 1.98–2.09 (m, 3H; H_{eq}-4,5,10), 1.42 (s, 2H; H_2O), 1.19–1.64 (m, 7H; H_{ax}-4,5,10, H-2″,3″), 0.93 (t, $^3J(H,H) = 7.4$ Hz, 3H; H-4″); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 5; further signals: $\delta = 143.9$ (s, C-4′), 137.1 (s, C-1′), 128.7 (d, C-3′), 125.4 (d, C-2′), 114.2, 113.5 (s, C≡N), 36.7 (t, C-10), 36.2, 35.9 (d, C-4a,10a), 35.4 (t, C-1″), 33.5 (t, C-2″), 29.9 (t, C-5), 29.6 (t, C-3), 28.8 (t, C-4), 28.0 (t, C-6), 22.3 (t, C-3″), 13.9 (q, C-4″); FT-IR (KBr): $\tilde{\nu} = 2215$ (s, C≡N), 1538 (vs), 1505 (vs), 1336 (m), 1185 (s), 912 cm^{-1} (m); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 380 (100) $[M]^+$, 337 (36); elemental analysis calcd (%) for $C_{27}H_{28}N_2 \cdot 0.5\,H_2O$ (389.5): C 83.25, H 7.50, N 7.19; found: C 83.32, H 7.39, N 6.93.

[2,3,4,4a,5,6,10,10a-Octahydro-7-(5-*n*-butyl-2-thienyl)-2-anthrylidene]methanedicarbonitrile (19b): According to the procedure described for **19a** the reaction was carried out with **18b** (0.4 g, 1.18 mmol), malonitrile (0.156 g, 2.36 mmol), the catalyst (0.05 g piperidine and 0.03 g HOAc in DMF, 2 mL) and DMF (15 mL) over a period of 18 h. After removal of solvent the residue was dissolved in $CHCl_3$ (100 mL), washed with water (50 mL with 3 mL of conc. HCl) and brine (2 × 80 mL). Drying ($MgSO_4$), removal of solvent, flash chromatography (100 g SiO_2; toluene/$CHCl_3$/ethyl acetate 15:2:1, $R_f = 0.46$) and extraction with boiling *n*-pentane afforded a red powder (0.157 g, 34%, m.p. 171 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.02$ (d, $^3J(H,H) = 3.7$ Hz, 1H; H-3′), 6.72 (d, $^3J(H,H) = 3.7$ Hz, 1H; H-4′), 6.54 (d, $^4J(H,H) = 1.7$ Hz, 1H; H-8), 6.52 (s, 1H; H-1), 6.14 (s, 1H; H-9), 2.98–3.02 (m, 1H; H_{eq}-3), 2.76–2.82 (m, 3H; H_{eq}-6, H-1″), 2.46–2.62 (m, 4H; H_{ax}-3,6, H-4a,10a), 1.96–2.05 (m, 3H; H_{eq}-4,5,10), 1.61–1.70 (m, 2H; H-2″), 1.35–1.53 (m, 4H; H_{ax}-4,5, H-3″), 1.24 (q, $^2J(H,H) = {}^3J(H,H) = 12.4$ Hz, 1H; H_{ax}-10), 0.94 (t, $^3J(H,H) = 7.4$ Hz, 3H; H-4″); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 5; further signals: $\delta = 148.1$ (s, C-5′), 142.0 (s, C-2′), 125.4 (d, C-4′), 125.2 (d, C-3′), 114.3, 113.6 (s, C≡N), 36.6 (t, C-10), 36.2 (d, C-4a), 35.8 (d, C-10a), 33.6 (t, C-2″), 30.1 (t, C-1″), 29.5 (t, C-3), 29.4 (t, C-5), 28.7 (t, C-4), 27.8 (t, C-6), 22.1 (t, C-3″), 13.8 (q, C-4″); FT-IR (KBr): $\tilde{\nu} = 2217$ (vs, C≡N), 1527 (vs), 1507 (vs), 1455 (s), 1448 (vs), 1338 (s), 1184 (s), 898 cm^{-1} (s); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 386 (100) $[M]^+$, 343 (44); elemental analysis calcd (%) for $C_{25}H_{26}N_2S$ (386.6): C 77.68, H 6.78, N 7.25, S 8.30; found: C 77.70, H 6.86, N 7.21, S 8.41.

[2,3,4,4a,5,6,10,10a-Octahydro-7-(4-*N*,*N*-dimethylaminophenyl)-2-anthrylidene]methanedicarbonitrile (19c): A solution of **18c** (0.24 g, 0.75 mmol) in anhydrous DMF (20 mL) was added to malonitrile (0.08 g, 1.21 mmol), piperidine (0.35 mL), acetic acid (0.15 mL) and acetic anhydride (0.2 mL) in DMF (3 mL) under a nitrogen atmosphere. After stirring for 24 h at 80 °C, the solvent was removed in vacuo and the residue was taken up in CH_2Cl_2 (150 mL). After washing with water (2 × 50 mL), drying ($MgSO_4$) and evaporation of solvent, the product was purified by flash chromatography (50 g SiO_2; toluene/$CHCl_3$/ethyl acetate 3:3:1, $R_f = 0.69$) and by

extraction with boiling EtOH. Drying in vacuo afforded **19c** (0.052 g, 19%) as blue microcrystals (m.p. 259°C). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.46-7.48$ (AA′ of AA′XX′, 2H; H-2′), 6.69–6.71 (XX′ of AA′XX′, 2H; H-3′), 6.65 (d, $^4J(H,H) = 1.9$ Hz, 1H; H-8), 6.53 (s, 1H; H-1), 6.16 (s, 1H; H-9), 3.02 (s, 6H; CH_3), 3.00–3.05 (m, 1H; H_{eq}-3), 2.80–2.85 (m, 1H; H_{eq}-6), 2.50–2.65 (m, 4H; H_{ax}-3,6, H-4a,10a), 1.97–2.07 (m, 3H; H_{eq}-4,5,10), 1.45–1.52 (m, 2H; H_{ax}-4,5), 1.25 (q, $^2J(H,H) = {}^3J(H,H) = 12.4$ Hz, 1H; H_{ax}-10); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): See Table 5; further signals: $\delta = 150.9$ (s, C-4′), 127.0 (s, C-1′), 126.7 (d, C-2′), 114.7, 113.9 (s, C≡N), 112.0 (d, C-3′), 40.3 (q, CH_3), 36.8 (t, C-10), 36.4, 36.1 (d, C-4a,10a), 30.0 (t, C-5), 29.6 (t, C-3), 28.9 (t, C-4), 27.7 (t, C-6); FT-IR (KBr): $\tilde{\nu} = 2220$ (s, C≡N), 1610 (s), 1521 (vs), 1509 (vs), 1374 (s), 1179 (s), 1167 (m), 901 (m), 822 cm^{-1} (m); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): (367) $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{25}N_3$ (367.5): C 81.71, H 6.86, N 11.43; found: C 81.80, H 6.96, N 11.27.

[2,3,4,4a,5,6,10,10a-Octahydro-7-(4-*N*,*N*-di-*n*-butylaminophenyl)-2-anthrylidene]methanedicarbonitrile (19d): As described for **19a**, the reaction of **18d** (0.16 g, 0.4 mmol), malonitrile (0.052 g, 0.79 mmol) and the catalyst (0.05 g piperidine and 0.03 g HOAc in DMF, 2 mL) was carried out in DMF (10 mL) over a period of 72 h. After aqueous workup as described in the previous experiment and flash chromatography (100 g SiO_2; $CHCl_3$/cyclohexane 1:1, $R_f = 0.38$), the product was extracted with boiling diethyl ether and the resulting solution was concentrated to about 5 mL. From this **19d** precipitated as dark blue powder (0.086 g, 76%, m.p. 231°C). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.43-7.45$ (AA′ of AA′XX′, 2H; H-2′), 6.63 (s, 1H; H-8), 6.61–6.63 (XX′ of AA′XX′, 2H; H-3′), 6.51 (s, 1H; H-1), 6.13 (s, 1H; H-9), 3.31 (t, $^3J(H,H) = 7.6$ Hz, 4H; H-1″), 2.98–3.14 (m, 1H; H_{eq}-3), 2.80–2.85 (m, 1H; H_{eq}-6), 2.47–2.62 (m, 4H; H_{ax}-3,6, H-4a,10a), 1.96–2.17 (m, 3H; H_{eq}-4,5,10), 1.42–1.62 (m, 6H; H_{ax}-4,5, H-2″), 1.32–1.41 (m, 4H; H-3″), 1.27 (q, $^2J(H,H) = {}^3J(H,H) = 12.4$ Hz, 1H; H_{ax}-10), 0.96 (t, $^3J(H,H) = 7.3$ Hz, 6H; H-4″); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): See Table 5; further signals: $\delta = 148.7$ (s, C-4′), 126.9 (d, C-2′), 125.6 (s, C-1′), 114.8, 114.0 (s, C≡N), 111.3 (d, C-3′), 50.7 (t, C-1″), 36.8 (t, C-10), 36.4 (d, C-4a), 36.1 (d, C-10a), 29.9 (t, C-5), 29.6 (t, C-3), 29.5 (t, C-2″), 28.9 (t, C-4), 27.6 (t, C-6), 20.3 (t, C-3″), 14.0 (q, C-4″); FT-IR (KBr): $\tilde{\nu} = 2209$ (vs, C≡N), 1607 (m), 1519 (vs), 1485 (vs), 1451 (s), 1361 (s), 1335 (s), 1326 (s), 1183 cm^{-1} (vs); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 451 (100) $[M]^+$, 408 (59), 366 (38), 352 (12); elemental analysis calcd (%) for $C_{31}H_{37}N_3$ (451.7): C 82.44, H 8.26, N 9.30; found: C 82.46, H 8.34, N 9.19.

[2,3,4,4a,5,6,10,10a-Octahydro-7-(5-piperidino-2-thienyl)-2-anthrylidene]-methanedicarbonitrile (19e): Malonitrile (5 × 0.025 g, 1.83 mmol) was added to a solution of **18e** (0.17 g, 0.47 mmol), HOAc (0.1 mL), Ac_2O (0.05 mL) and piperidine (0.6 mL) in dry DMF (20 mL) over a period of 44 h at 80°C. Aqueous workup (vide supra), flash chromatography (50 g SiO_2; $CHCl_3$, $R_f = 0.18$) and extraction with boiling EtOH afforded **19e** as blue microcrystals (0.098 g, 51%, m.p. 238–240°C). ^{1}H NMR (400 MHz, $CDCl_3$ 25°C, TMS): $\delta = 6.97$ (d, $^3J(H,H) = 4.1$ Hz, 1H; H-4′), 6.46 (s, 1H; H-1), 6.30 (s, 1H; H-8), 6.06 (s, 1H; H-9), 5.97 (d, $^3J(H,H) = 4.1$ Hz, 1H; H-3′), 3.24 (t, $^3J(H,H) = 5.5$ Hz, 4H; H-2″), 2.96 (ddd, $^2J(H,H) = 17.6$ Hz, $^3J(H,H) = 3.8$, 2.3 Hz, 1H; H_{eq}-3), 2.78 (ddd, $^2J(H,H) = 17.5$ Hz, $^3J(H,H) = 4.7$, 2.2 Hz, 1H; H_{eq}-6), 2.45–2.52 (m, 4H; H_{ax}-3,6, H-4a,10a), 1.93–2.02 (m, 3H; H_{eq}-4,5,10), 1.69–1.74 (m, 4H; H-3″), 1.59–1.64 (m, 2H; H-4″), 1.41–1.51 (m, 2H; H_{ax}-4,5), 1.24 (q, $^2J(H,H) = {}^3J(H,H) = 12.4$ Hz, 1H; H_{ax}-10); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): See Table 5; further signals: $\delta =$ 161.1 (s, C-5′), 128.4 (s, C-2′), 127.4 (d, C-3′), 115.0, 114.2 (s, C≡N), 104.4 (d, C-4′), 51.1 (t, C-2″), 36.8 (t, C-10), 36.4 (d, C-4a), 36.2 (d, C-10a), 29.5 (2 × t, C-3,5), 28.9 (t, C-4), 27.3 (t, C-6), 25.0 (t, C-3″), 23.7 (t, C-4″); FT-IR (KBr): $\tilde{\nu} = 2211$ (s, C≡N), 1538 (s), 1506 (s), 1470 (s), 1440 (s), 1182 cm^{-1} (s); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 413 (100) $[M]^+$; elemental analysis calcd (%) for $C_{26}H_{27}N_3S$ (413.6): C 75.51, H 6.58, N 10.16, S 7.75; found: C 75.33, H 6.63, N 10.00, S 7.74.

7-Piperidino-2,3,4,4a,5,6,10,10a-octahydroanthracen-2-one (20): Sodium hydride (suspension in oil, ca. 50%, 0.240 g, ca. 5 mmol) was added in small portions under a nitrogen atmosphere to a solution of **12b** (1.46 g, 4.19 mmol) and piperidine (0.5 mL, 5.06 mmol) in anhydrous acetonitrile (20 mL). After stirring for 30 h at 70°C the mixture was cooled to 25°C and water (5 mL) was added. After removal of the solvent, the residue was taken up in $CHCl_3$ (150 mL). After filtration, the filtrate was washed with water (100 mL) and dried (Na_2SO_4). Then the solvent was removed, and the residue was purified by flash chromatography (100 g SiO_2; toluene/$CHCl_3$/ethyl acetate 3:3:2, $R_f = 0.27$). The collected fractions containing pure **20** were carefully concentrated to about 10 mL of mainly toluene. From this **20** (0.363 g, 31%) crystallised analytically pure as small yellow needles (m.p. 240°C; part. decomp). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 5.77$ (s, 1H; H-9), 5.65 (s, 1H; H-1), 5.34 (s, 1H; H-8), 3.15–3.41 (m, 4H; H-2′), 2.28–2.58 (m, 6H; H-3,4a,6,10a), 1.89–2.06 (m, 3H; H_{eq}-4,5,10), 1.58–1.76 (m, 7H; H_{ax}-4, H-3′,4′), 1.44 (dq, $^2J(H,H) = {}^3J(H,H) = 12.7$ Hz, $^3J(H,H) = 5.0$ Hz, 1H; H_{ax}-5), 1.24 (q, $^2J(H,H) = {}^3J(H,H) = 12.3$ Hz, 1H; H_{ax}-10); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): See Table 5; further signals: $\delta = 47.5$ (t, C-2′), 37.7 (t, C-3), 37.0 (t, C-10), 36.3 (d, C-4a), 35.8 (d, C-10a), 30.5 (t, C-4), 30.1 (t, C-5), 27.7 (t, C-6), 25.4 (t, C-3′), 24.4 (t, C-4′); FT-IR (KBr): $\tilde{\nu} = 1622$ (s, C=O), 1549 (vs), 1527 (vs), 1173 cm^{-1} (vs); UV/Vis: See Table 1; MS (70 eV, EI): *m*/*z* (%): 283 (100) $[M]^+$; elemental analysis calcd (%) for $C_{19}H_{25}NO$ (283.4): C 80.52, H 8.89, N 4.94; found: C 80.41, H 8.89, N 4.91.

2-(1,3-Diethyl-2-thioxodihydropyrimidine-4,6-dionylidene)-7-piperidino-2,3,4,4a,5,6,10,10a-octahydroanthracene (21): *N*,*N*-Diethylthiobarbituric acid (1.94 g, 9.69 mmol) and **20** (0.55 g, 1.94 mmol) were heated under reflux in the presence of 2,2,6,6- tetramethylpiperidine (0.1 mL, 0.59 mmol) in anhydrous toluene (50 mL) for 3 d with a Dean-Stark trap under a nitrogen atmosphere. After cooling the solvent was removed, and the residue was subjected to flash chromatography (200 g SiO_2; $CHCl_3$/EtOH 20:1, $R_f = 0.34$). The product was further purified by extraction with boiling diethyl ether. After 12 h the obtained green solution was discarded and the extraction was continued with fresh solvent. From this **21** precipitated as dark green solid that was dried at 80°C in vacuo for 12 h (0.564 g, 63%, m.p. 261°C). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.92$ (s, 1H; H-1), 6.08 (s, 1H; H-9), 5.75 (s, 1H; H-8), 4.52–4.65 (m, 4H; N-CH_2-), 3.57–3.58 (m, 4H; H-2″), 3.37 (ddd, $^2J(H,H) = 18.9$ Hz, $^3J(H,H) = 3.9$, 2.5 Hz, 1H; H_{eq}-3), 2.87–2.96 (m, 1H; H_{ax}-3), 2.69 (ddd, $^2J(H,H) = 17.4$ Hz, $^3J(H,H) = 4.8$, 1.9 Hz, 1H; H_{eq}-6), 2.42–2.57 (m, 3H; H-4a,10a, H_{ax}-6), 2.02–2.06 (m, 1H; H_{eq}-5), 1.88–1.93 (m, 2H; H_{eq}-4,10), 1.73–1.75 (m, 6H; H-3″,4″), 1.41–1.58 (m, 2H; H_{ax}-4,5), 1.31 (t, $^3J(H,H) = 6.9$ Hz, 6H; CH_3), 1.24 (q, $^2J(H,H) = {}^3J(H,H) = 12.3$ Hz, 1H; H_{ax}-10); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): See Table 5; further signals: $\delta = 176.3$ (s, C=S), 161.3 (s, C=O), 49.1 (t, C-2″), 43.1 (t, N-CH_2-), 37.0 (d, C-4a), 36.7 (t, C-10), 35.9 (d, C-10a), 32.5 (t, C-3), 30.7 (t, C-4), 29.0 (t, C-5), 28.1 (t, C-6), 26.3 (t, C-3″), 23.9 (t, C-4″), 12.9 (q, CH_3); FT-IR (KBr): $\tilde{\nu} = 1644$ (s, C=O), 1610 (s), 1463 (s), 1440 (s), 1372 (s), 1310 (vs), 1157 (vs), 1144 (s), 1112 (s) 1098 (vs), 1000 cm^{-1} (s); UV/Vis: See Table 1; (DMSO): λ_{max} (ε) = 624 nm (87200 dm^{3}mol^{-1}cm^{-1}); MS (70 eV, EI): *m*/*z* (%): 465 (100) $[M]^+$, 432 (63); elemental analysis calcd (%) for $C_{27}H_{35}N_3O_2S$ (465.7): C 69.64, H 7.58, N 9.02, S 6.89; found: C 69.62, H 7.56, N 9.00, S 6.82.

(7-Piperidino-2,3,4,4a,5,6,10,10a-octahydroanthracen-2-ylidene)piperidinium perchlorate (22): Trimethyloxonium tetrafluoroborate (0.282 g, 1.91 mmol) was added in small portions to a stirred solution of **20** (0.45 g, 1.59 mmol) in anhydrous CH_2Cl_2 (30 mL) at 0°C over a period of about 1 min. The bright yellow solution changed immediately to orange. After stirring and warming to 25°C over 15 h, diethyl ether (70 mL) was added dropwise and the dark yellow precipitate (0.498 g) was collected by vacuum filtration, dried in vacuo and used without further purification. This intermediate (0.4 g) was suspended in anhydrous pyridine (5 mL), piperidine (0.2 mL, 2.02 mmol) was added in the same solvent (2 mL), and a change of colour from yellow to red was observed. After addition of triethylamine (0.7 mL, 5.02 mmol) the mixture was heated to reflux for 3 h. Most of the pyridine was removed by distillation, and the residue was dissolved in $CHCl_3$ (50 mL), shaken with a solution of $HClO_4$ (60%, 3 mL) in water (50 mL), and washed with aqueous $NaClO_4$ solution (30%, 3 × 20 mL) and deionised water (50 mL). After removal of solvent, the product was purified by flash chromatography (50 g SiO_2). Toluene/$CHCl_3$/ethyl acetate (5:2:1) as eluent gave remaining **20** and then the solvent was changed to $CHCl_3$/EtOH 10:1 for elution of **22**, $R_f = 0.44$. Soluble impurities were removed from the solid product by extraction with boiling diethyl ether (3 h), and pure **22** was obtained as small blue needles after extraction with boiling methanol and concentration of the resulting dark red solution to about 5 mL (0.278 g, ca. 48%, m.p. 216–217°C). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 5.94$ (s, 1H; H-9), 5.75 (s, 2H; H-1,8), 3.57–3.65 (m, 8H; H-2′,2″), 2.78 (ddd, $^2J(H,H) = 17.2$ Hz, $^3J(H,H) = 4.8$, 2.0 Hz, 2H; H_{eq}-3,6), 2.47–2.57 (m, 4H; H_{ax}-3,6, H-4a,10a), 2.08–2.13 (m, 2H; H_{eq}-4,5), 1.99 (dt, $^2J(H,H) = 12.5$ Hz, $^3J(H,H) = 4.3$ Hz, 1H; H_{eq}-10), 1.69–1.82 (m, 12H; H-3′,3″,4′,4″), 1.52 (dq, $^2J(H,H) = 12.9$ Hz, $^3J(H,H) = 4.9$ Hz, 2H; H_{ax}-4,5), 1.24 (q, $^2J(H,H) = {}^3J(H,H) = 12.3$ Hz, 1H; H_{ax}-10);

0947-6539/02/0807-1588 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 7

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 5; further signals: $\delta = 48.9$ (t, C-2′,2″), 35.9 (t, C-10), 35.6 (d, C-4a,10a), 29.0 (t, C-4,5), 27.9 (t, C-3,6), 26.2 (t, C-3′,3″), 24.0 (t, C-4′,4″); FT-IR (KBr): $\tilde{\nu} = 1496$ (vs), 1483 (vs), 1465 (s), 1446 (vs), 1337 (vs), 1176 (vs), 1089 (vs), 1005 (s), 890 cm^{-1} (vs); UV/Vis: See Table 1; (DMSO): λ_{max} (ε) = 540 nm (217000 $dm^3 mol^{-1} cm^{-1}$); MS (FAB, pos, NBA): *m*/*z* (%): 351 (100) $[M]^+$; elemental analysis calcd (%) for $C_{24}H_{35}N_2ClO_4$ (451.0): C 63.92, H 7.82, N 6.21; found: C 63.87, H 7.90, N 5.81.

(2,3,4,4a,5,6,10,10a-Octahydro-7-piperidino-2-anthrylidene)methanedicarbonitrile (23): By the same procedure as described for **17**, the reaction was carried out with **14** (material for synthetic purposes, (vide supra), 0.92 g, ca. 2.2 mmol), piperidine (0.27 mL, 2.73 mmol) and sodium hydride (suspension in oil, ca. 50%, 0.134 g, ca. 2.79 mmol) in anhydrous CH_3CN (20 mL). After heating to reflux for 14 h, cooling, addition of water (5 mL) and removal of solvent, the residue was taken up in $CHCl_3$ (100 mL) and filtrated, and the filtrate was washed with water (100 mL, with a few drops of conc. HCl). The aqueous phase was extracted with $CHCl_3$ (50 mL) and the combined organic solutions were washed with water (3 × 100 mL). Drying ($MgSO_4$), removal of solvent, flash chromatography (100 g SiO_2; toluene/$CHCl_3$/ethyl acetate 10:2:1, $R_f = 0.24$) and extraction with boiling MeOH afforded **23** as blue microcrystals (0.305 g, ca. 42%, m.p. 258 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.19$ (s, 1H; H-1), 5.74 (s, 1H; H-9), 5.41 (s, 1H; H-8), 3.28–3.37 (m, 4H; H-2′), 2.82 (ddd, ^2J(H,H) = 17.4 Hz, ^3J(H,H) = 4.1, 2.2 Hz, 1H; H_{eq}-3), 2.50 (ddd, ^2J(H,H) = 16.7 Hz, ^3J(H,H) = 4.8, 2.1 Hz, 1H; H_{eq}-6), 2.27–2.44 (m, 4H; H_{ax}-3,6, H-4a,10a), 1.82–1.95 (m, 3H; H_{eq}-4,5,10), 1.54–1.64 (m, 6H; H-3′,4′), 1.32–1.46 (m, 2H; H_{ax}-4,5), 1.16 (q, ^2J(H,H) = ^3J(H,H) = 12.3 Hz, 1H; H_{ax}-10); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): See Table 5; further signals: $\delta = 117.1$, 116.2 (s, C≡N), 47.8 (t, C-2′), 36.7 (t, C-10), 36.6 (d, C-4a), 35.7 (d, C-10a), 29.7 (t, C-5), 29.4 (t, C-3), 29.2 (t, C-4), 27.7 (t, C-6), 25.8 (t, C-3′), 24.3 (t, C-4′); FT-IR (KBr): $\tilde{\nu} = 2187$ (s, C≡N), 1490 (vs), 1463 (vs), 1445 (vs), 1420 (vs), 1328 (vs), 1268 (s), 1171 (vs), 1162 (s), 1124 (vs), 1007 cm^{-1} (vs); UV/Vis: See Table 1; (DMSO): λ_{max} (ε) = 594 nm (248000 $dm^3 mol^{-1} cm^{-1}$); MS (70 eV, EI): *m*/*z* (%): 331 (100) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{25}N_3$ (331.5): C 79.72, H 7.60, N 12.68; found: C 79.69, H 7.62, N 12.56.

Acknowledgements

The DFWM experiments were carried out in the laboratories of Prof. M. Schwoerer, University of Bayreuth. We thank the Bundesministerium für Bildung und Forschung (BMBF) for generous financial support.

[1] J. J. Wolff, R. Wortmann, *J. Prakt. Chem.* **1998**, *340*, 99–111.
[2] a) G. Bourhill, J.-L. Brédas, L.-T. Cheng, S. R. Marder, F. Meyers, J. W. Perry, B. G. Tiemann, *J. Am. Chem. Soc.* **1994**, *116*, 2619–2620; b) R. Ortiz, S. R. Marder, L.-T. Cheng, B. G. Tiemann, S. Cavagnero, J. W. Ziller, *J. Chem. Soc. Chem. Commun.* **1994**, 2263–2264; c) S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J.-L. Brédas, B. M. Pierce, *Science* **1994**, *265*, 632–635.
[3] a) F. Meyers, S. R. Marder, B. M. Pierce, J.-L. Brédas, *J. Am. Chem. Soc.* **1994**, *116*, 10703–10714; b) C. B. Gorman, S. R. Marder, *Chem. Mater.* **1995**, *7*, 215–220.
[4] M. Del Zoppo, C. Castiglioni, V. Gerola, P. Zuliani, G. Zerbi, *J. Opt. Soc. Am. B* **1998**, *15*, 308–317.
[5] S. Beckmann, K.-H. Etzbach, P. Krämer, K. Lukaszuk, R. Matschiner, A. J. Schmidt, P. Schuhmacher, R. Sens, G. Seybold, R. Wortmann, F. Würthner, *Adv. Mater.* **1999**, *11*, 536–541.
[6] M. Blanchard-Desce, R. Wortmann, S. Lebus, J.-M. Lehn, P. Krämer, *Chem. Phys. Lett.* **1995**, *243*, 526–532.
[7] a) I. N. Zhmurova, Y. L. Slominskii, A. I. Tolmachev, R. I. Yurchenko, *Zh. Obshch. Khim.* **1969**, *39*, 1732–1736; *Russ. J. Gen. Chem.* **1969**, *39*, 1697–1701; b) Y. L. Slominskii, A. L. Skul'bidenko, A. I. Tolmachev, *Zh. Org. Khim.* **1975**, *11*, 392–397; *Russ. J. Org. Chem.* **1975**, *11*, 383–387; c) G. Heilig, W. Lüttke, *Chem. Ber.* **1986**, *119*, 3102–3108.
[8] G. Heilig, W. Lüttke, *Chem. Ber.* **1987**, *120*, 1863–1866.
[9] a) C.-F. Shu, W. J. Tsai, J.-Y. Chen, A. K.-Y. Jen, Y. Zhang, T.-A. Chen, *Chem. Commun.* **1996**, 2279–2280; b) C.-F. Shu, W. J. Tsai, A. K.-Y. Jen, *Tetrahedron Lett.* **1996**, *37*, 7055–7058; c) C. Zhang, A. S. Ren, F. Wang, J. Zhu, L. R. Dalton, J. N. Woodford, C. H. Wang, *Chem. Mater.* **1999**, *11*, 1966–1968.
[10] a) I. Cabrera, O. Althoff, H.-T. Man, H. N. Yoon, *Adv. Mater.* **1994**, *6*, 43–45; b) Y.-C. Shu, Z.-H. Gong, C.-F. Shu, E. M. Breitung, R. J. McMahon, G.-H. Lee, A. K.-Y. Jen, *Chem. Mater.* **1999**, *11*, 1628–1632.
[11] C.-F. Shu, Y.-C. Shu, Z.-H. Gong, S.-M. Peng, G.-H. Lee, A. K.-Y. Jen, *Chem. Mater.* **1998**, *10*, 3284–3286.
[12] U. Lawrentz, W. Grahn, I. Dix, P. G. Jones, *Acta Crystallogr. Sect. C* **1999**, *55*, 446–450.
[13] B. Kippelen, S. R. Marder, E. Hendrickx, J. L. Maldonado, G. Guillemet, B. L. Volodin, D. D. Steele, Y. Enami, Sandalphon, Y. J. Yao, J. F. Wang, H. Röckel, L. Erskine, N. Peyghambarian, *Science* **1998**, *279*, 54–57.
[14] E. Hendrickx, B. D. Günther, Y. Zhang, J. F. Wang, K. Staub, Q. Zhang, S. R. Marder, B. Kippelen, N. Peyghambarian, *Chem. Phys.* **1999**, *245*, 407–415.
[15] W. Grahn, U. Lawrentz, K. Lukaszuk, R. Wortmann, A. Feldner, D. Scherer, M. Schwoerer, J. Bendig, S. Helm, I. Dix, P. G. Jones, *Proc. SPIE Int. Soc. Opt. Eng.* **1999**, *3796*, 247–256.
[16] S. Dähne, *Chimia* **1991**, *45*, 288–296.
[17] P. Maslak, A. Chopra, C. R. Moylan, R. Wortmann, S. Lebus, A. L. Rheingold, G. P. A. Yap, *J. Am. Chem. Soc.* **1996**, *118*, 1471–1481.
[18] a) M. Barzoukas, C. Runser, A. Fort, M. Blanchard-Desce, *Chem. Phys. Lett.* **1996**, *257*, 531–537; b) M. Blanchard-Desce, M. Barzoukas, *J. Opt. Soc. Am. B* **1998**, *15*, 302–307.
[19] J. A. Marshall, N. H. Andersen, *J. Org. Chem.* **1965**, *30*, 1292–1294.
[20] R. E. Schmidt, B. Stein (I. G. Farbenindustrie), DRP 497503, **1930** [*Chem. Abstr.* **1930**, *24*, 3251].
[21] Farbwerke Höchst, DRP 77818, **1893** [*Chem. Zentralbl.* **1895**, *66*, 247].
[22] E. L. Martin, *J. Am. Chem. Soc.* **1936**, *58*, 1438–1442.
[23] W. F. Gannon, H. O. House, W. E. Parham, W. E. Noland, G. Meisters, A. M. Huffmann, *Org. Synth.* **1960**, *40*, 41–42.
[24] A. Carotti, G. Casini, M. Ferappi, G. M. Cingolani, *J. Heterocycl. Chem.* **1980**, *17*, 1577–1584.
[25] R. Lemke, *Synthesis* **1974**, 359–361; a great variety of conditions for the Knoevenagel reaction were used throughout this work, as results could not be reproduced in several cases.
[26] a) J. E. McMurry, W. J. Scott, *Tetrahedron Lett.* **1983**, *24*, 979–982; b) A. G. Martínez, R. Martínez Alvarez, M. Madueño Casado, L. R. Subramanian, M. Hanack, *Tetrahedron* **1987**, *43*, 275–279.
[27] *Organikum*, 18th ed., Deutscher Verlag der Wissenschaften, Berlin, **1990**, p. 559.
[28] a) A.-C. Guevel, D. J. Hart, *J. Org. Chem.* **1996**, *61*, 473–479; b) C. J. Kowalski, K. W. Fields, *J. Org. Chem.* **1981**, *46*, 197–201.
[29] H. Meerwein, W. Florian, N. Schön, G. Stopp, *Justus Liebigs Ann. Chem.* **1961**, *641*, 1–39.
[30] a) W. Liptay in *Excited States*, *Vol. 1* (Ed.: E. C. Lim), Academic Press, New York, **1974**, pp. 129–229; b) W. Baumann, *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 231–240; c) F. Würthner, F. Effenberger, R. Wortmann, P. Krämer, *Chem. Phys.* **1993**, *173*, 305–314; d) R. Wortmann, P. Krämer, C. Glania, S. Lebus, N. Detzer, *Chem. Phys.* **1993**, *173*, 99–108.
[31] a) F. Würthner, S. Yao, J. Schilling, R. Wortmann, M. Redi-Abshiro, E. Mecher, F. Gallego-Gomez, K. Meerholz, *J. Am. Chem. Soc.* **2001**, *123*, 2810–2824; b) F. Würthner, R. Wortmann, R. Matschiner, K. Lukaszuk, K. Meerholz, Y. DeNardin, R. Bittner, C. Bräuchle, R. Sens, *Angew. Chem.* **1997**, *109*, 2933–2936; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2765–2768.
[32] J. L. Oudar, D. S. Chemla, *J. Chem. Phys.* **1977**, *66*, 2664–2668.
[33] R. Wortmann, C. Poga, R. J. Twieg, C. Geletneky, C. R. Moylan, P. M. Lundquist, R. G. DeVoe, P. M. Cotts, H. Horn, J. E. Rice, D. M. Burland, *J. Chem. Phys.* **1996**, *105*, 10637–10647.
[34] C. R. Moylan, R. Wortmann, R. J. Twieg, I.-H. McComb, *J. Opt. Soc. Am. B* **1998**, *15*, 929–932.
[35] M. Welscher, Degree thesis, University of Bayreuth (Germany), **1998**.
[36] P. P. Ho, R. R. Alfano, *Phys. Rev. A.* **1979**, *20*, 2170–2187.
[37] a) C. Castiglioni, M. Gussoni, M. Del Zoppo, G. Zerbi, *Solid State Commun.* **1992**, *82*, 13–17; b) M. Del Zoppo, C. Castglioni, G. Zerbi, M. Rui, M. Gussoni, *Synth. Met.* **1992**, *51*, 135–146; c) M. Rumi, G. Zerbi, K. Müllen, G. Müller, M. Rehahn, *J. Chem. Phys.* **1997**, *106*, 24–34; d) P. Zuliani, M. Del Zoppo, C. Castiglioni, G. Zerbi, C. Andraud, T. Brotin, A. Collet, *J. Phys. Chem.* **1995**, *99*, 16242–16247.

[38] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed., VCH, Weinheim, **1988**, pp. 408 – 411.
[39] R. Radeglia, S. Dähne, H. Hartmann, *J. Prakt. Chem*. **1970**, *312*, 1081 – 1086.
[40] V. Alain, L. Thouin, M. Blanchard-Desce, U. Gubler, C. Bosshard, P. Günter, J. Muller, A. Fort, M. Barzoukas, *Adv. Mater*. **1999**, *11*, 1210 – 1214.
[41] S. R. Marder, C. B. Gorman, B. G. Tiemann, L.-T. Cheng, *J. Am. Chem. Soc.* **1993**, *115*, 3006 – 3007.
[42] M. Klessinger, *Chem. Unserer Zeit* **1978**, *12*, 1 – 11, and references therein.
[43] a) R. Radeglia, R. Wolff, B. Bornowski, S. Dähne, *J. Prakt. Chem.* **1981**, *323*, 125 – 128; b) U. Lawrentz, unpublished result.
[44] H. Ma, A. K.-Y. Jen, J. Wu, X. Wu, S. Liu, C.-F. Shu, L. R. Dalton, S. R. Marder, S. Thayumanavan, *Chem. Mater.* **1999**, *11*, 2218 – 2225.
[45] R. Wortmann, D. M. Bishop, *J. Chem. Phys.* **1998**, *108*, 1001 – 1007.
[46] C. Bubeck in *Electronic Materials: The Oligomer Approach* (Eds.: G. Wegner, K. Müllen), VCH Weinheim, New York, Chichester, Brisbane, Singapore, Toronto, **1998**, pp. 449 – 478.
[47] C. W. Dirk, L.-T. Cheng, M. G. Kuzyk, *Int. J. Quant. Chem.* **1992**, *43*, 27 – 36.
[48] A. Feldner, D. Scherer, M. Welscher, T. Vogtmann, M. Schwoerer, U. Lawrentz, T. Laue, H.-H. Johannes, W. Grahn, *Nonlinear Opt.* **2000**, *26*, 99 – 106.
[49] G. Scheibe, W. Seiffert, G. Hohlneicher, C. Jutz, H. J. Springer, *Tetrahedron Lett.* **1966**, *41*, 5053 – 5059.
[50] a) I. Baraldi, S. Ghelli, Z. A. Krasnaya, F. Momicchioli, A. S. Tatikolov, D. Vanossi, G. Ponterini, *J. Photochem. Photobiol. A* **1997**, *105*, 297 – 305; b) M. Blanchard-Desce, V. Alain, P. V. Bedworth, S. R. Marder, A. Fort, C. Runser, M. Barzoukas, S. Lebus, R. Wortmann, *Chem. Eur. J.* **1997**, *3*, 1091 – 1104.
[51] R. Radeglia, G. Engelhardt, E. Lippmaa, T. Pehk, K.-D. Nolte, S. Dähne, *Org. Magn. Reson.* **1972**, *4*, 571 – 576.
[52] S. Dähne, D. Leupold, *Ber. Bunsenges. Phys. Chem*. **1966**, *70*, 618 – 625.
[53] L. Hellermann, C. C. Porter, H. J. Lowe, H. F. Koster, *J. Am. Chem. Soc.* **1946**, *68*, 1890 – 1893.
[54] H. Hartmann, S. Scheithauer, *J. Prakt. Chem*. **1969**, *311*, 827 – 843.

Received: May 14, 2001
Revised: September 27, 2001 [F3254]

  0947-6539/02/0807-1590 $ 20.00+.50/0