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Synthesis of Ethyl 3-Aryl-1-methyl-8-oxo-8*H*-anthra[9,1-*gh*]quinoline-2-carboxylates as Dyes for Potential Application in Liquid Crystal Displays

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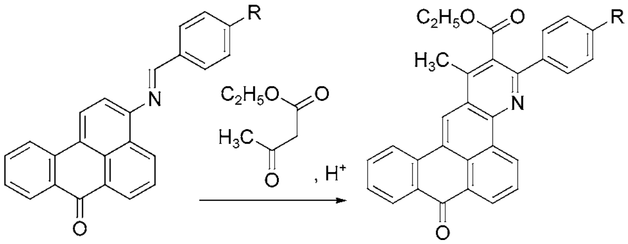
ABSTRACT



Two new fluorescent ethyl 3-aryl-1-methyl-8-oxo-8*H*-anthra[9,1-*gh*]quinoline-2-carboxylates have been synthesized for the first time by cyclization of 3-(arylidene-amino)-benzo[*de*]anthracen-7-ones with 3-oxo-butyric acid ethyl ester. The cyclization reaction was investigated with and without concentrated hydrochloric acid as a catalyst. New dyes have shown a very good orientation parameter (S_A) in nematic liquid crystal, indicating a high potential for application in liquid crystal displays.

Benzo[*de*]anthracen-7-one (benzanthrone) derivatives are interesting compounds due to their excellent color characteristics and high photostability.[1] They have been widely used as dyes for polymers[2] and textiles,[3] daylight fluorescent pigments,[4] and laser dyes.[5] With a view to obtaining compounds with new and extraordinary photo- or electrochemical properties some pyridino-1-azabenzanthrones have been synthesized by Skraup synthesis of the corresponding amino-1-azabenzanthrones.[6]

It has been shown that some 3-oxy- and 3-amino-substituted benzanthrone derivatives are suitable luminophores for use in nematic liquid crystals (LC) for electro-optical displays of the “guest−host” type.[7] Recently, 3-azomethine-substituted benzanthrones **1** were synthesized and the new compounds showed satisfactory LC properties because of their elongated molecular structures.[8] Their action is based on the so-called “guest−host” effect, which consists of orienting the LC molecules under applied voltage accompanied by close alignment of dye molecules, with the resulting selectivity in dye absorption depending upon orientation.[9] Among the most important problems at the practical utilization of this type of display is the choice of suitable fluorescent dyes.

For our further work it was of interest to synthesize benzanthrone derivatives with elongated and planar molecule structures whose long molecular axis will shift toward the

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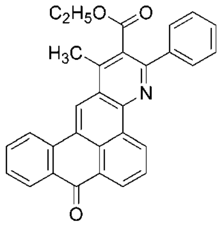
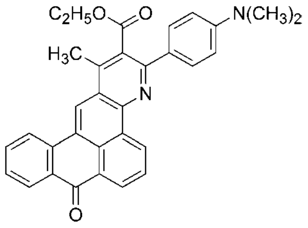
absorption transition moment and is parted by better orientation in nematic LC. In this Letter we report the synthesis of ethyl 1-methyl-3-phenyl-8-oxo-8*H*-anthra[9,1-*gh*]quinoline-2-carboxylate (**2a**) and ethyl 3-(4-(dimethylamino)-phenyl)-1-methyl-8-oxo-8*H*-anthra[9,1-*gh*]quinoline-2-carboxylate (**2b**) and their potential as dichroic dyes for application in LC displays.



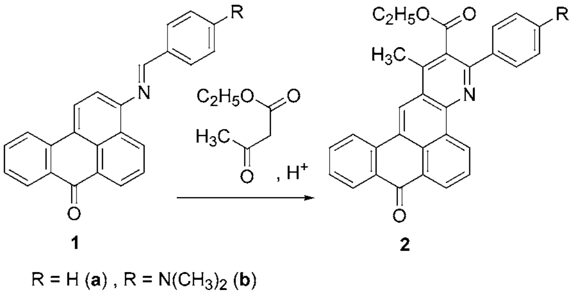
2a



2b

The synthesis of 3-aryl-1-methyl-8-oxo-8*H*-anthra[9,1-*gh*]-quinoline-2-carboxylic acid ethyl esters **2** is displayed in Scheme 1. Azomethines **1a** and **1b** were prepared by condensation of 3-amino-benzo[*de*]anthracen-7-one with aromatic aldehydes according to the reported procedures.[8] The starting 3-amino-benzo[*de*]anthracen-7-one was obtained by subsequent nitration and reduction of the commercially available benzanthrone.[10]

Scheme 1



Fluorescent dyes **2** were synthesized by a cyclization reaction of 3-(arylidene-amino)-benzo[*de*]anthracen-7-ones **1** with excess of 3-oxo-butyric acid ethyl ester. The cyclization reaction was investigated in both the presence and the absence of concentrated hydrochloric acid. In the presence of a catalytic amount of concentrated hydrochloric acid the desired compounds **2a** and **2b** were obtained in 40−43% yields (Table 1).[11]

New compounds **2** were characterized by their melting points, TLC (R_f values), UV/vis, and fluorescence spectra (Table 1) and identified by elemental analysis data and FT-IR, ^1H NMR, and ^{13}C NMR spectra.[12]

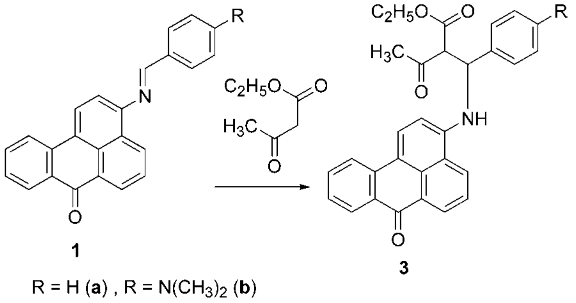
Table 1. Yields and Characteristic Data of 3-Aryl-1-methyl-8-oxo-8*H*-anthra[9,1-*gh*]quinoline-2-carboxylic Acid Ethyl Esters **2**

	2a	**2b**
yield, %	40	43
mp, °C	133−135	166−168
R_f[a]	0.56	0.67
λ_A, nm[b]	466	478
log ϵ	4.02	4.17
λ_F, nm[c]	532	546

[a] TLC on silica gel, Fluka F_{60} 254, 20 × 20, 0.2 mm, using as eluant the solvent system *n*-heptane:acetone (1:1). [b] The electronic spectra of dyes **2** in dichloromethane were recorded on a Hewlett-Packard 8452A spectrophotometer with 2-nm resolution, at room temperature. [c] The fluorescence spectra of dyes **2** in dichloromethane at a concentration of 10^{-6} mol L^{-1} were recorded on a Perkin-Elmer MPF 44 spectrophotometer at room temperature.

The investigations on the interaction of azomethines **1** with 3-oxo-butyric acid ethyl ester in the absence of hydrochloric acid showed that under these conditions the reaction leads to noncycled compounds **3** (Scheme 2).

Scheme 2



In the FT-IR spectra of **3** there are characteristic bands at 3384−3378 and 1706−1702 cm^{-1} for the aromatic imino group (NH) and the ketone carbonyl group (C═O), respectively, which are absent in the FT-IR spectra of the catalytic reaction products **2**. Similar data were observed also in the ^1H and ^{13}C NMR spectra of compounds **3**.[13]

The noncycled compounds **3** were cyclized in the desired products **2** in boiling ethanol in the presence of concentrated hydrochloric acid (Scheme 3). Final dyes **2** were obtained in relatively lower yield to the catalyzed reaction (Scheme 1) yields (23−26%).[14]

On the basis of these results it can be concluded that the anthraquinoline ring system formation in the synthesis of dyes **2** gets through the noncycled 3-oxo-2-[(7-oxo-7*H*-benzo[*de*]anthracen-3-ylamino)-aryl-methyl]-butyric acid

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(10) Rody, J.; Rytz, G.; Slongo, M. Eur. Patent 0 328 024, 1989, CIBA G. AG; *Chem. Abstr.* **1990**, *112*, 100755z.

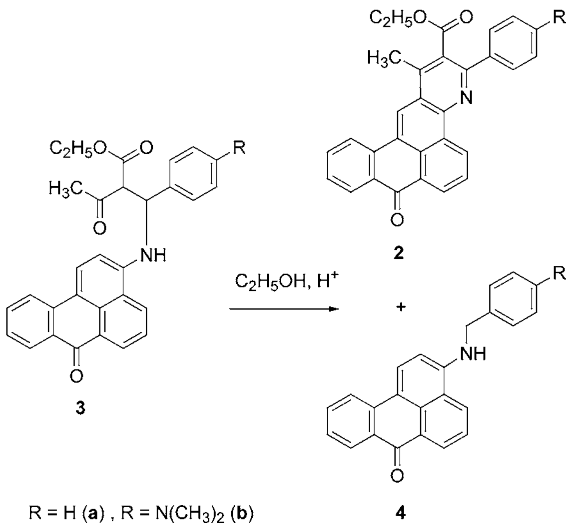
(11) A detailed description of the preparation procedures for compounds **2a** and **2b** in the presence of a catalytic amount of hydrochloric acid is provided in the Supporting Information.

(12) The elemental analysis and spectral data for dyes **2a** and **2b** are provided in the Supporting Information.

(13) The preparation procedure, elemental analysis, and FT-IR, ^1H NMR, and ^{13}C NMR spectral data for noncycled compounds **3a** and **3b** are provided in the Supporting Information.

(14) The preparation procedure for cyclization of compounds **3** to dyes **2** in the presence of hydrochloric acid is available in the Supporting Information.

Scheme 3



ethyl esters **3**. It should be noted that along with the final dyes **2** at the cyclization reaction 3-benzylamino-benzo[*de*]-anthracen-7-ones **4** were isolated (Scheme 3).[15] Thereby, it has been experimentally demonstrated for the first time that the azomethine **1** operates as a proton acceptor during the anthraquinoline ring system formation.

The applicability of the new fluorescent dyes **2** for coloring LC displays of the guest−host type was examined on the basis of their orientation in surface-stabilized display cells.[16] Particularly convenient for measuring orientation parameters in LC systems involving dichroic dyes is the method based on polarized absorption or fluorescence spectra.

The orientation order parameter S_A of a dye in LC can be calculated by use of eq 1.[17]

$$S_A = \frac{A^{||} - A^{\perp}}{A^{||} + 2A^{\perp}}\left(1 - \frac{3}{2}\sin^2\beta\right)^{-1} \tag{1}$$

Here, $A^{||}$ and $A^{\perp}$ are the corresponding absorbencies in polarized light (at λ_{max}) at parallel and vertical orientations of the polarizer toward the LC director, and β is the angle between the long molecular axis of the dye and the vector of its absorption transition moment. At $\beta = 0$, eq 1 reduces to eq 2.[18]

$$S_A = \frac{A^{||} - A^{\perp}}{A^{||} + 2A^{\perp}} \equiv \frac{N(\lambda) - 1}{N(\lambda) + 2} \tag{2}$$

Here, $N(\lambda) = A^{||}/A^{\perp}$ is the dichroic ratio of the dye molecule in polarized light.

It is accepted that elongation of dye molecules enables their better orientation in LC. Table 2 displays the values of the dichroic ratio $N(\lambda)$ and the orientation parameter S_A of the new dyes **2** compared to those of azomethines **1** synthesized before.[7a,8b]

Table 2. Spectral Characteristics, Dichroic Ratio, $N(\lambda_A)$, and Orientation Order, S_A, of Azomethines **1** and Dyes **2** in LC

	1a[7a]	**1b**[8b]	**2a**	**2b**
λ_A, nm	438	458	468	482
$N(\lambda_A)$	4.54	4.62	6.37	6.89
S_A	0.54	0.55	0.64	0.67
λ_F, nm			528	540

The data presented in Table 2 showed the potential of the novel dyes **2** for use in LC systems for displays. The fluorescence emission of the dyes in the nematic liquid crystal ZLI 1840 is retained and their orientation parameters S_A determined were higher than those of noncycled azomethines **1**, which is surely connected with the nearly planar structure that compounds **2a** and **2b** exhibit in LC. The better orientation value for dye **2b** may alternatively be related to the electron-donating nature of the substituent NMe_2.

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Supporting Information Available: Experimental details and characterization of the synthesized compounds **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] The isolation procedure and characterization data for 3-benzylamino-benzo[*de*]anthracen-7-ones **4a** and **4b** are provided in the Supporting Information.

[16] Commercial LC ZLI 1840 (Merck) was used as host material, which exhibits a stable nematic phase over a broad temperature range.

[17] Ivashchenko, A.; Petrova, O.; Titov, V. *Mol. Cryst. Liq. Cryst*. **1984**, *108*, 51.

[18] UV neutral filters were used for recording the polarized absorption spectra. The long molecular axis of dyes **2** is shifted by definition toward the direction of the absorption transition moment.