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Short Note

3-[*N*-(4-Methoxybenzyl)amino]benzo[*de*]anthracen-7-one

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Abstract: Herein, we describe the synthesis of 3-[*N*-(4-methoxybenzyl)amino]benzo[*de*]anthracen-7-one via a two-step procedure including 3-aminobenzanthrone condensation with anisaldehyde and following reduction of obtained imine to appropriate amine by sodium borohydride. The structure of the synthesized compounds was established by elemental analysis, nuclear magnetic resonance spectroscopy, mass spectrometry (EI-MS), and infrared spectroscopy (FT-IR) and confirmed by single-crystal X-ray diffraction. The title compound was analyzed by thermal gravimetric analysis, UV/vis, and fluorescence spectroscopy.

Keywords: 3-aminobenzanthrone; azomethine; reduction; secondary amine; fluorescent dye

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1. Introduction

Amines are one of the most important classes of substances in organic chemistry and lead to the production of many compounds for various applications in science and industry. 3-Aminobenzantrone is an aromatic primary amine that is both a luminescent dye and a starting material for the synthesis of other nitrogen-containing compounds. A number of azomethines have been derived from amines [1–3] by condensation with aromatic aldehydes. Several of the obtained imines have been proposed as suitable components for "guest-host" liquid-crystal systems for electro-optic displays.

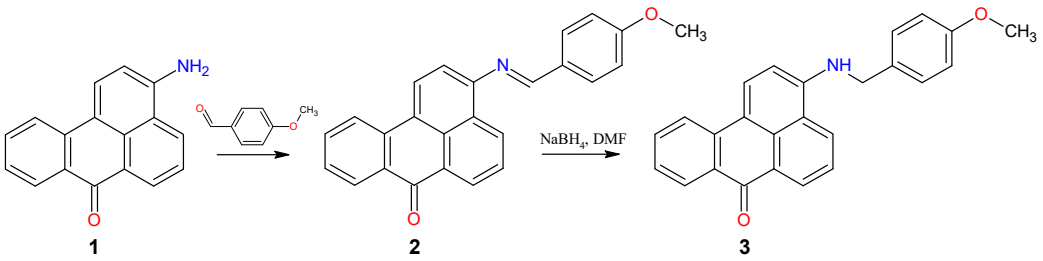
Secondary amines can be obtained from imines by their reduction. The reduction of azomethines to the corresponding amines is one of the most widely used functional group transformations in synthetic organic chemistry because amine derivatives play crucial roles in various applications in synthetic chemistry and biology [4].

Based on previous research and following our interest in the design of emissive benzanthrone dyes, the aim of the present work is to create a new luminescent amino derivative of benzanthrone. Previously, heterocyclic imines and amines of benzanthrone were synthesized and characterized [5]. Continuing these studies, new derivatives were obtained by coupling of 3-aminobenzanthrone with anisaldehyde, followed by reduction with sodium borohydride. The obtained compounds were fully characterized, including the determination of the structure by single-crystal X-ray diffraction analysis and photophysical parameters in various media.

2. Results and Discussion

2.1. Synthesis

In connection with our current interest on the synthesis of luminescent compounds for bio-visualization and sensing purposes [5–8], we report a two-step synthesis of novel substituted amino derivatives of benzanthrone through a condensation reaction between 3-aminobenzanthrone and excess of anisaldehyde to form the azomethine 2, followed by reduction with sodium borohydride in DMF with methanol as a catalyst (at ambient temperature), as depicted in Scheme 1.



Scheme 1. Synthesis of 3-[*N*-(4-methoxybenzyl)amino]benzo[*de*]anthracen-7-one (3).

We decided to carry out the synthesis of imine **2** without solvent because we found that the reaction of initial amine **1** in excess of aldehyde led to the formation of Schiff base **2** in a high yield (80%). In the ^{1}H-NMR spectrum of the obtained imine, there are singlets of the methoxy group at 3.86, multiplet of aromatic protons (nine protons of benzanthrone residue and four protons of 4-methoxyphenyl group) at 6.98–8.78 ppm, and a singlet at 8.50 ppm of the azomethine proton (see Supplementary Materials).

Sodium borohydride was chosen to reduce azomethine **2** to amine, because it is an inexpensive, safe-to-handle, and environmentally friendly reducing agent [9]. The reduction of the prepared imine with $NaBH_4$ as hydride ion donor, in the presence of methanol as the catalyst, resulted in the preparation of 3-[*N*-(4-methoxybenzyl)amino]benzo[*de*]anthracen-7-one (**3**) at 82% yield. This is a new compound with absorptions in FT-IR at 3385 cm^{-1} for the newly formed NH group. The ^{1}H-NMR spectrum of the synthesized amine **3** showed a broad signal at 5.11 ppm assigned to the NH proton, a doublet at 4.45 ppm (J = 4.7 Hz, 2H) associated with the methylene protons, and the absence of a singlet at 8.50 ppm of the imine proton (CH=N), which indisputably confirmed the reduction of the imine 2 generated by the condensation reaction of amine **1** with p-methoxybenzaldehyde.

The newly obtained imine **2** turned out to be unstable, which made it impossible to identify the molecular ion for it after passing through the chromatographic column. Ions with M-1 and M-2 were found for amine **3** (see Supplementary Figure S8).

By analyzing the DTA/TG curve (see Supplementary Materials), it can be concluded that the amino derivative is more thermally stable than azomethines, since amines lose 5% of their weight at about 340 °C, in comparison with azomethine, which loses 5% of its weight at about 220 °C.

2.2. Spectroscopic Properties

The photophysical properties of the synthesized azomethine and amine were evaluated, and the corresponding data are summarized in Table 1. The absorption and emission spectra were recorded in seven organic solvents with a wide range of polarities. Fluorescence spectra were recorded under excitation at 425 nm (for compound **2**) and 480 nm (for compound **3**). The starting 3-aminobenzanthrone is characterized by absorption at 460–530 nm and by luminescence at 560–670 nm and is used as an orange-red luminophore and laser dye [10].

Table 1. Photophysical parameters of studied derivatives in various solvents.

Solvent	Absorption λ_{abs} (lgε), nm		Fluorescence λ_{em}, nm	
	Imine 2	Amine 3	Imine 2	Amine 3
Benzene	429 (4.58)	482 (4.66)	561	567
Ethyl acetate	425 (4.58)	491 (4.69)	581	588
Chloroform	434 (4.59)	489 (4.70)	500	600
Acetone	428 (4.58)	502 (4.77)	500	612
DMF	434 (4.59)	514 (4.72)	500	621
DMSO	437 (4.62)	524 (4.73)	511	635
Ethanol	436 (4.32)	520 (4.64)	540	658

The absorption peak of imine 2 is hypsochromically shifted by 40–80 nm in comparison with starting amine 1, showing a long-wavelength band at 420–440 nm, the position of which is practically independent of the solvent polarity. The absorption spectra of the synthesized amine 3 have a broad long-wave intense absorption band at 480–525 nm. The emission spectra of the synthesized amine have maxima at 560–660 nm, strongly depending on the solvent polarity, unlike azomethine, which has an emission with low intensity at 500–560 nm.

2.3. X-ray Crystallographic Study

For compound **3,** the crystal structure was determined using the single-crystal X-ray crystallographic method. Figure 1 gives a perspective view of molecular structure **3** with thermal ellipsoids and the atom-numbering scheme followed in the text. In the molecules, the benzanthrone fragment is characterized by planar conformation. The torsion angle of C3–N18–C19–C20 is equal −88.8(6)°. This leads to the fact that the benzanthrone system and the plane of the benzene ring are almost perpendicular. It should be noted that the crystal structure is chiral (space group P21), although there are no asymmetric atoms in the molecule. Obviously, substance **3** represents a mixture of enantiomorphous crystals (racemic mixture), where there are also crystals present in the structure, of which there are molecules with the value of C3–N18–C19–C20 torsion angle of +88.8 degrees.

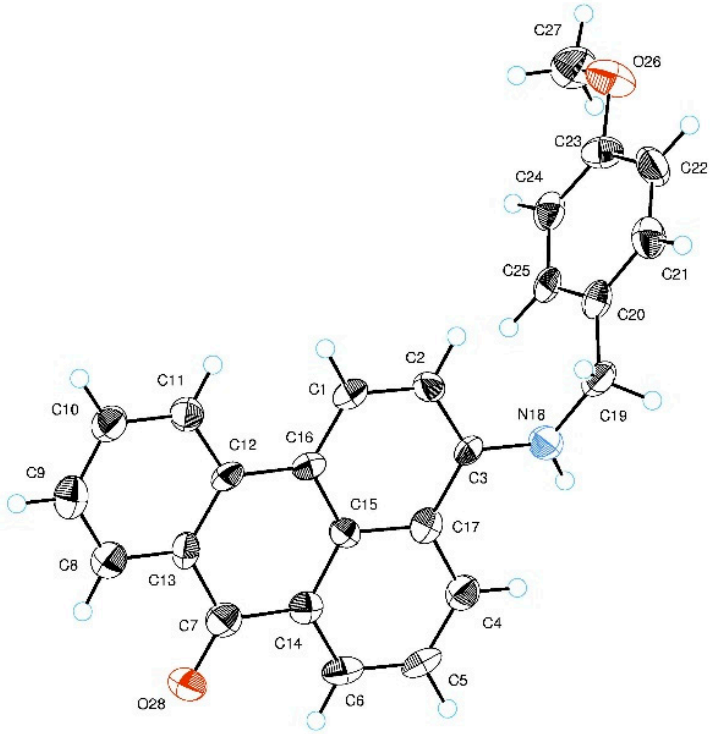


Figure 1. ORTEP diagram of molecule **3**.

In the crystal structure, a moderate intermolecular hydrogen bond of the NH···O type is found. The length of this bond is 3.014(6) Å (H···O = 2.18(5) Å, N–H···O = 159(4)°). By means of these bonds, the molecular chains are formed in the crystal structure (see Figure 2). In the crystals, there are also weak intermolecular π-π stacking interactions between benzanthrone systems with the shortest atom–atomic (C4···C16) contact of 3.407(7) Å. By means of these interactions, the molecules are packed, forming stacks along the smallest lattice parameter a.

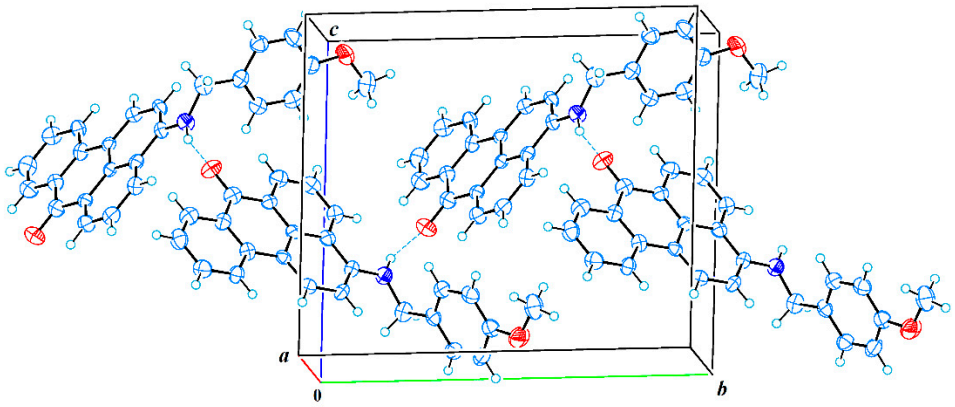


Figure 2. Formation of the molecular chain in the crystals **3**.

3. Materials and Methods

3.1. Materials and Basic Measurements

All reagents were of analytical grade (Aldrich Chemical Company, Munich, Germany) and were used as received. The progress of the chemical reactions and the purity of products were monitored by TLC on silica gel plates (Fluka F60254, 20 × 10, 0.2 mm, ready-to-use), using C_6H_6–CH_3CN (3:1) as eluent and visualization under UV light. Column chromatography on silica gel was carried out on Merck Kieselgel (230–240 mesh), with dichloromethane as eluent. Melting points were determined on an MP70 Melting Point System apparatus and are not corrected.

The identification of the chemical bonds was performed by means of Fourier-transform infrared (FT-IR) spectrometry (Bruker, Billerica, MA, USA). A Bruker Vertex 70v vacuum spectrometer equipped with an attenuated total reflection (ATR) accessory was used in this study. At least 3 spectra per sample were measured with a recording range of 400–4000 cm^{-1}, spectral resolution ±2 cm^{-1}, in vacuum 2.95 hPa, and the average spectrum was calculated from the measured spectra. ^{1}H NMR spectra were recorded on Bruker equipment (Bruker, Billerica, MA, USA), operating at 400 MHz in $CDCl_3$ (with TMS as internal standard) at ambient temperature. ^{13}C NMR spectra were run in the same instrument at 100 MHz, using the solvent (DMSO-d_6) peak as the internal reference. Elemental analysis was performed on a Euro Vector EA-3000 CHNS-analyzer (Pavia, Italy).

The absorption spectra were obtained using the UV–visible spectrophotometer "Specord's UV/VIS" (Analytik Jena AG, Jena, Germany). Fluorescence spectra were recorded on an FLSP920 (Edinburgh Instruments Ltd., Edinburgh, United Kingdom) spectrofluorometer in the visible range of 500–800 nm. The studies were performed in quartz cuvettes with an absorbing layer thickness of 1 cm at a concentration of solutions in organic solvents of 10^{-5} mol/L.

Simultaneous TG-DTA and DSC curves were collected using a Exstar6000 TG/DTA (Seiko Instruments Inc., Tokyo, Japan) 6300 thermal analyzer with a heating rate of 10 K min^{-1} in temperature interval 30–400 °C with sample masses of approximately 5 mg. Aluminum crucibles were used for analysis.

3.2. Synthesis and Characterization

3-Aminobenzanthrone (1) was prepared by nitration of benzanthrone and subsequent reduction of the obtained 3-nitroderivative according to the literature procedure [11].

3.2.1. 3-[*N*-(4-Methoxybenzyledene)amino]benzo[*de*]anthracen-7-one (2)

3-Aminobenzo[*de*]anthracen-7-one (**1**) (245 mg, 1.0 mmol) and p-methoxybenzaldehyde (5 mL) were placed in a round-bottom flask, and the resulting mixture was heated in a oil bath at 110–120 °C for 4 h. The reaction mixture was cooled to room temperature. The resulting precipitate was filtered off and washed with methanol, recrystallized from benzene and dried to obtain pure compound 3 in 80% yield as a yellow solid (m.p. 189 °C).

FT-IR (KBr): 3054, 2924, 2844, 1650, 1598, 1574 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 3.86 (s, 3H), 6.98–7.01 (m, 2H), 7.46 (dt, J = 7.6; 1.0 Hz, 1H), 7.66–7.79 (m, 3H), 7.93–7.96 (m, 2H), 8.27 (dt, J = 8.1, 0.7 Hz, 1H), 8.45–8.47 (m, 2H), 8.50 (s, 1H), 8.74–8.78 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 56.2, 110.4, 111.8, 114.8, 123.6, 124.2, 125.3, 126.9, 127.7, 127.9, 128.1, 128.7, 129.4, 130.1, 130.2, 132.0, 134.3, 136.4, 149.6, 151.3, 152.9, 162.2, 183.2. Anal. calcd. for $C_{25}H_{17}NO_2$: C, 82.63; H, 4.72; N, 3.85; found: C, 82.16; H, 4.39; N, 3.71.

3.2.2. 3-[*N*-(4-Methoxybenzyl)amino]benzo[*de*]anthracen-7-one (3)

3-[*N*-(4-Methoxybenzyledene)amino]benzo[*de*]anthracen-7-one (2) (183 mg, 0.5 mmol) was dissolved in 15 mL of N,N-dimethylformamide, and 0.5 mmol (0.019 g) of NaBH4 was added in small portions over 15 min. A 2–3 mL volume of of methanol was added dropwise to the solution prepared at room temperature. The reaction mixture was stirred at room temperature in an ultrasonic bath for 5–6 h, monitoring the reaction by thin layer chromatography in benzene: acetonitrile 3:1. The product obtained was precipitated with water and washed with methanol, recrystallized from benzene, and dried. The product was obtained as a red crystalline solid with a yield of 82% (m.p. 218–220 °C). FT-IR (KBr): 3385, 2928, 2828, 1634, 1567, 1540 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 3.85 (s, 3H), 4.45 (d, J = 4.7 Hz, 2H), 5.11 (br. s, 1H), 6.70 (d, J = 8.2 Hz, 1H), 6.88 (dd, J = 5.9, 2.3 Hz, 2H), 7.32–7.37 (m, 3H), 7.59–7.66 (m, 2H), 8.13–8.17 (m, 2H), 8.25 (d, J = 8.2 Hz, 1H), 8.41 (dd, J = 7.8, 1.2 Hz, 1H), 8.76 (dd, J = 7.4, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 45.5, 55.8, 105.1, 113.6, 122.5, 122.9, 123.1, 125.0, 126.3, 127.4, 128.3, 128.5, 128.7, 128.8, 129.7, 130.0, 133.8, 137.4, 147.6, 148.9, 150.1, 183.0. Anal. calcd. for $C_{25}H_{19}NO_2$: C, 82.17; H, 5.24; N, 3.83; found: C, 82.01; H, 5.07; N, 3.69. EI-MS m/z 364 $[M-1]^+$ (31), 363 $[M-2]^+$ (100), 348 (4), 334 (7), 319 (20), 291 (9), 256 (7), 227 (10), 201 (22), 181 (29).

3.3. Single-Crystal X-ray Analysis

A suitable crystal 0.43 mm × 0.07 mm × 0.02 mm was selected and mounted on a suitable support on a Bruker–Nonius KappaCCD diffractometer (Bruker, Billerica, Massachusetts, USA) with Mo Kα radiation (λ = 0.71073 Å). The crystal was kept at a steady T = −100 °C during data collection. The crystal structure was solved with the help of SHELXS structure solution program [12]. The model was refined with the program SHELXL using full-matrix least squares method [12].

Crystal Data: C25H19NO2, Mr = 365.41, monoclinic, P21 (No. 4), a = 5.1595(4) Å, b = 13.9950(9) Å, c = 12.479(1) Å, β = 94.725(3)°, V = 898.0(1) Å3, Z = 2, Z′ = 1, μ(Mo Kα) = 0.086 mm^{-1}, 2912 reflections measured, 2361 unique which were used in all calculations. The final wR2 was 0.1496 (all data), and R1 was 0.0664 (for 1337 reflections with $I \geq 2\sigma(I)$).

For further details, see crystallographic data for three deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication Number CCDC 2106683. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

4. Conclusions

We demonstrated an efficient method for the synthesis of 3-amino-substituted benzanthrone using reduction of azomethine derived from 3-aminobenzanthrone The structure of obtained compounds was confirmed by element analysis, NMR, and FT-IR spectroscopy. Single-crystal structures of synthesized amine were determined by X-ray diffraction studies. Target aminoderivative has bright solvatochromic fluorescence in organic solvents showing positive fluorosolvatochromism, which can be further used for probing the polarity of the environment in chemistry and biology.

Supplementary Materials: The following are available online, Figure S1: Solutions of synthesized amine 3 in benzene, ethyl acetate, chloroform, dimethylformamide, dimethyl sulfoxide, and ethanol in visible and UV light (365 nm); Figure S2: ^{1}H NMR spectrum of 3-[*N*-(4-methoxybenzyledene)amino] benzo[*de*]anthracen-7-one (2); Figure S3: ^{1}H NMR spectrum of 3-[*N*-(4-methoxybenzyl)amino]

benzo[*de*]anthracen-7-one (3); Figure S4: Simultaneous TG-DTA curves for 3-[*N*-(4-methoxybenzyledene) amino]benzo[*de*]anthracen-7-one (2); Figure S5: Simultaneous TG-DTA curves for 3-[*N*-(4-methoxybenzyl) amino]benzo[*de*]anthracen-7-one (3); Figure S6: The absorption and emission (l_{exc} = 425 nm) spectra of 3-[*N*-(4-methoxybenzyledene)amino]benzo[*de*]anthracen-7-one (2) in various organic solvents; Figure S7: The absorption and emission (l_{exc} = 500 nm) spectra of 3-[*N*-(4-methoxybenzyl)amino] benzo[*de*]anthracen-7-one (3) in various organic solvents; Figure S8: Mass spectrum of 3-[*N*-(4-methoxybenzyl)amino]benzo[*de*]anthracen-7-one (3); Figure S9: ^{13}C NMR spectrum of 3-[*N*-(4-methoxybenzyledene)amino]benzo[*de*]anthracen-7-one (2); Figure S10: ^{13}C NMR spectrum of 3-[*N*-(4-methoxybenzyl)amino]benzo[*de*]anthracen-7-one (3); Table S1: Crystal data and structure refinement parameters for 3-[*N*-(4-methoxybenzyl)amino]benzo[*de*]anthracen-7-one (3); Table S2: Bond lengths and angles for 3-[*N*-(4-methoxybenzyl)amino]benzo[*de*]anthracen-7-one (3).

Author Contributions: A.K. and E.K. designed chemical synthesis, analyzed results, and wrote the manuscript. A.P. performed spectroscopic experiments and analyzed results. S.B. performed single-crystal X-ray diffraction analysis and wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds 2 and 3 are available from the authors.

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