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## Photophysical characteristics of three novel benzanthrone derivatives: Experimental and theoretical estimation of dipole moments

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### ABSTRACT

The effect of solvents on absorption and fluorescence spectra and dipole moments of novel benzanthrone derivatives such as 3-*N,N'*-Dimethylformamidino) benzanthrone (1), 3-*N,N'*-Diethylacetamidino) benzanthrone (2) and 3-morpholinobenzanthrone (3) have been studied in various solvents. The fluorescence lifetime of the dyes (1–3) in chloroform were also recorded. Bathochromic shift observed in the absorption and fluorescence spectra of these molecules with increasing solvent polarity indicates that the transitions involved are  $\pi \rightarrow \pi^*$ . Using the theory of solvatochromism, the difference in the excited-state ( $\mu_e$ ) and the ground-state ( $\mu_g$ ) dipole moments was estimated from Lippert–Mataga, Bakhshiev, Kawski–Chamma–Viallet, and McRae equations by using the variation of Stokes shift with the solvent's relative permittivity and refractive index. AM1 and PM6 semiempirical molecular calculations using MOPAC and ab-initio calculations at B3LYP/6-31  $G^*$  level of theory using Gaussian 03 software were carried out to estimate the ground-state dipole moments and some other physicochemical properties. Further, the change in dipole moment value ( $\Delta\mu$ ) was also calculated by using the variation of Stokes shift with the molecular-microscopic empirical solvent polarity parameter ( $E_T^N$ ). The excited-state dipole moments observed are larger than their ground-state counterparts, indicating a substantial redistribution of the  $\pi$ -electron densities in a more polar excited state for all the systems investigated.

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### 1. Introduction

Compounds containing donor and acceptor functionalities in conjugation are called push–pull systems. Substituted benzanthrone derivatives bearing electron-withdrawing groups on one carbon atom and electron-donating groups on the other also form a part of push–pull systems. The molecular structures and IUPAC names of the molecules under study are presented in Fig. 1. In present systems, the electron-donating substituent is at a C-3 position and the

carbonyl group of the chromophorous system is an electron-accepting group. These systems have interesting chemical and spectral properties. It is well-known, that for such systems electronic excitation is often accompanied by considerable charge redistribution. Intramolecular charge redistribution upon electronic excitation is a fundamental physicochemical process. A very fruitful and widely used method to study this process is the determination of electric dipole moments in different electronic states [1].

A dipole moment represents a direct measure of electron distribution in a molecule of known geometry. It is a physical constant which can be obtained by experimental and theoretical methods. A number of excellent texts, monographs, and reviews devoted to

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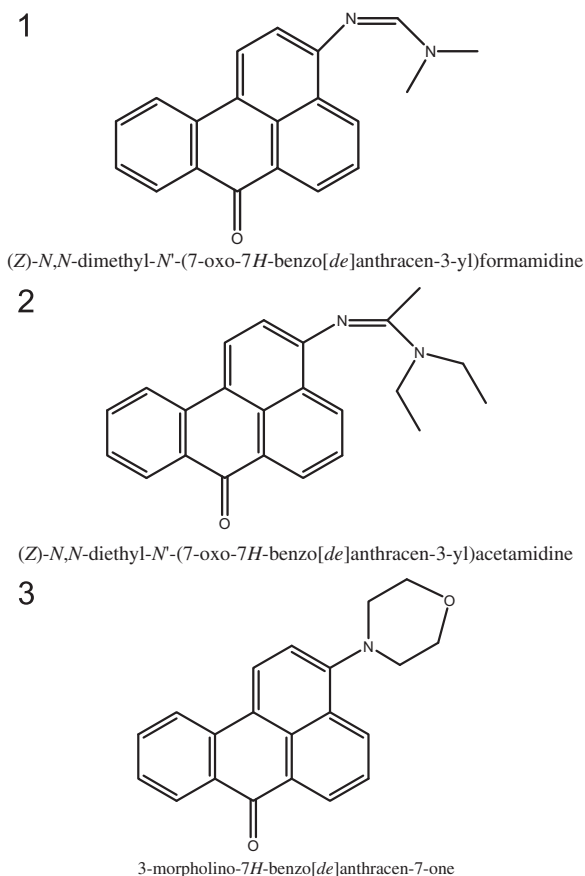


Fig. 1. Molecular structures of (1), (2) and (3) along with IUPAC names.

dipole moments are available and contain a detailed discussion of the theory of dipole moments [2–7]. Although most of these references are not recent, they have served as an excellent source of information and a starting point for this article. It seems worthwhile to point out here that, prior to the development and widespread applications of modern spectroscopic techniques, dipole moments represented one of the most important sources of structural information about organic molecules. Examples of the various practical applications of dipole moments include, but are not limited to: differentiation between isomers (cis and trans, o, m, and p, tautomers, etc.), conformational analysis, studies of molecular geometry, supporting evidence for resonance hybrids, information about the polar character of molecules (important for solubility in different solvents and permeability through membranes), information about electrical effects of substituents (inductive, resonance), studies of hydrogen bonding and electron donor–acceptor interactions (e.g., charge transfer complexes).

Experimental ground-state ( $\mu_g$ ) dipole moments can be obtained in different ways. The first and most widely used approach is based on the measurement of dielectric constants. The second group of methods utilizes microwave spectroscopy and molecular beams [8–10] (the Stark effect method, the molecular beam method, the electric resonance method, Raman spectroscopy, etc.).

Experimental methods for the determination of excited-state dipole moments are based on experimental ground-state dipole moments and a change of the position of a spectral band (in an electronic spectrum) caused by an electric field which can be external (electrochromism) or internal (solvatochromism). Electrooptical methods (electrochromism) are more accurate but are experimentally more difficult as they include electric polarization of fluorescence or phosphorescence [11], electric dichroism [12] and microwave conductivity [13], and absorption spectra in the vapor phase in an electric field (Stark effect). The solvatochromic methods (solvent-shift methods) are experimentally much simpler and widely accepted as they do not use any external field [8,14].

From the extensive literature survey it is evident that there are several recent reports published on experimental and theoretical studies on the ground-state ( $\mu_g$ ) and excited-state ( $\mu_e$ ) dipole moments using the solvatochromic method applied to variety of organic fluorescent compounds [15–23]. The benzanthrone derivatives such as 3-N-(N',N'-Dimethylformamidino) benzanthrone (1), 3-N-(N',N'-Diethylacetamidino) benzanthrone (2) and 3-morpholinobenzanthrone (3) whose dipole moments presented in this article are strongly fluorescent and their fluorescence properties are dependent on the surrounding environments. That is why they are widely used as a laser dye [24], daylight fluorescent pigment [25] and lipophilic fluorescent probe for biochemical and medicinal investigations [26,27].

## 2. Experimental

Novel benzanthrone derivatives (1–3) were synthesized as per the scheme published in our earlier articles [28,29]. All the solvents were procured from Aldrich Chemical Company and were used as received. The concentration of the solutions was maintained at  $10^{-5}$  M. The absorption spectra were recorded on Spectord's UV–visible spectrophotometer. The fluorescence emission spectra were obtained using Spectrofluor JY3 (ISA Jobin Yvon instruments S. A.). Fluorescence lifetimes of the fluorophores (1–3) in chloroform were measured using a time-correlated-single-photon-counting (TCSPC) spectrofluorometer [30] (model IBH DataStation Hub, Glasgow, UK). TCSPC is a digital technique, counts the photons, which are time correlated with the excitation pulse. The heart of the method is a time-to-amplitude converter (TAC). The sample is repetitively excited using a pulsed light source. In the present work we have used a 464 nm LED (frequency 1 MHz) as the excitation source and a TBX4 detection module coupled with a special Hamamatsu PMT for the fluorescence detection. The detector is having a spectral response from ~300 to 800 nm. Each pulse was optically monitored by a high-speed photodiode, to produce a start signal, which is used to trigger the voltage ramp of the TAC. The voltage ramp is stopped when the first fluorescence photon from the sample is detected. The TAC provides an output pulse whose voltage is proportional to the time between the start and stop signals. A multichannel analyzer (MCA)

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