

Synthesis, spectroscopic investigations and computational study of 4-((9,10-dioxo-9,10-dihydroanthracen-1-yl)oxy)benzaldehyde

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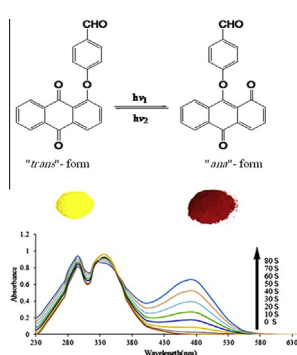
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HIGHLIGHTS

- Synthesis 4-((9,10-dioxo-9,10-dihydroanthracen-1-yl)oxy)benzaldehyde for the first time.
- IR, ¹H NMR ¹³C NMR, UV spectra and NBO analysis were reported.
- The first order hyperpolarizability and HOMO, LUMO energy gap are theoretically predicted.
- Thermodynamic properties and their correlations with temperature have been obtained.
- Transition structures were calculated by QST3 approach and yielded the potential energy surfaces.

GRAPHICAL ABSTRACT



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ABSTRACT

The molecular structure, vibrational frequencies, corresponding vibrational assignments of 4-((9,10-dioxo-9,10-dihydroanthracen-1-yl)oxy)benzaldehyde in “*trans*” and “*ana*” forms have been investigated by UV–Vis, FT-IR and NMR spectroscopy as well as density functional theory (DFT) B3LYP method with 6-311++G(d,p) basis set. The vibrational analysis of the two forms of cited compound was performed by means of infrared absorption spectroscopy in combination with theoretical simulations. The obtained geometrical parameters and wavenumbers of vibrational normal modes from the DFT method were in good consistency with the experimental values. The ¹H and ¹³C nuclear magnetic resonance (NMR) chemical shifts of the molecule were calculated by GIAO method. Computed molecular orbital and time dependent DFT oscillator renderings agree closely with experimental observations. The stability of the molecule arising from hyper-conjugative interaction and charge delocalization has been analyzed using NBO analysis. In order to predict the reactive sites, a molecular electrostatic potential map (MEP) for the title compound was obtained. Transition structures were calculated by QST3 and IRC methods which yielded the potential energy surface and activation energy.

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1. Introduction

Photochromism is characterized by photo-induced reversible isomerization of one isomer to another isomer which has a differ-

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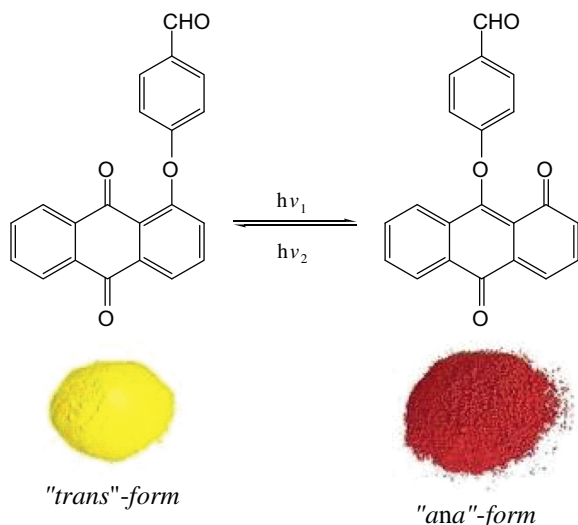
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ent absorption spectrum. Photochromic materials are potentially useful for advanced optoelectronic devices such as rewritable optical memory, optical switching, ophthalmic lenses, dental filling materials, chemical sensing, and color displays [1–3]. Among the different categories of photochromic materials, aryloxanthraquinone (AAQ) derivatives have greatly considered due to their outstanding exclusive properties such as low fatigue, bi-stability, and small thermal interconversion at ambient conditions [4]. The

photochromic reaction of AAQs involves photoinduced reversible aryl group migration process. The “*trans*” quinone isomer undergoes photochemical rearrangement of the π -bond system to form the “*ana*”-quinone isomer upon irradiation with UV light (Scheme 1) [5–7]. It was found that this process is photochemically and thermally reversible, as well as represents a new type of photochromic reaction of substituted AQs [8–10]. Also, photochemical migration of hydrogen, or acyl groups from *trans*-quinoid to the *ana*-quinoid structure was investigated [9–10]. Stability of “*ana*” and “*trans*” forms at ambient temperature is required for technical application of aryloxyquinones [11,12]. Natural and synthetic 9,10-AAQs show a wide spectrum of biological activities [13–16].

The theoretical *ab initio* and normal coordinate analysis give information regarding to the nature of the electronic structure, the functional groups, orbital interactions and mixing of skeletal frequencies. The structural characteristics and vibrational spectroscopic analysis of title compound by the quantum mechanical *ab initio* and DFT methods have not been studied. Thus, extensive experimental and theoretical studies were carried out on “*trans*” and “*ana*” forms to obtain a complete, reliable and accurate vibrational assignments and structural characteristics of the compound. *Ab initio* quantum mechanical method is widely used for simulating IR spectrum [17,18]. Time-dependent DFT (TD-DFT) calculations have also been used for the analysis of the electronic spectrum and spectroscopic properties. The energies, degrees of hybridization, populations of the lone electron pairs of nitrogen, energies of their interaction with the anti-bonding π^* orbitals, electron density (ED) distributions and $E^{(2)}$ energies have been calculated by NBO analysis using DFT method to give clear evidence of stabilization originating from the hyperconjugation of various intra-molecular interactions. In this work, IR, ^1H , ^{13}C NMR parameters and UV–Vis spectrum of “*trans*” and “*ana*” forms are reported experimentally and theoretically.

Theoretically calculated HOMO and LUMO energies are closely associated to oxidation potentials and reduction potentials of molecules. As stated by Koopman’s theorem [19], ionization energy is equal to the HOMO energy of a molecule, but of opposite sign, with the consequence that oxidation potentials may be related to HOMO energies. The electron located in the HOMO orbital is removed during oxidation. In a similar way LUMO energy is related to reduction potentials. Both HOMO and LUMO energies may readily be calculated, i.e. by means of DFT and other computational methods, as extensively discussed elsewhere [20].



Scheme 1. Photochromic reaction of aryloxyanthraquinones (AAQs).

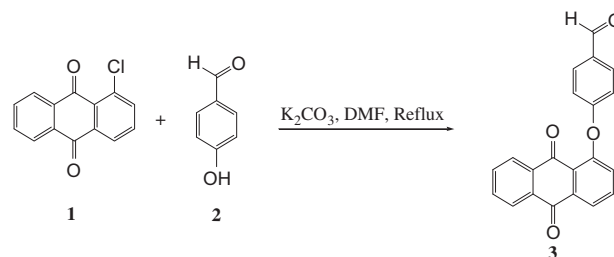
There has been growing interest in using organic materials for nonlinear optical (NLO) devices, functioning as second harmonic generators, frequency converters, electro-optical modulators, etc. Since the second order electric susceptibility is related to first hyperpolarizability, the search for organic chromophores with large first hyperpolarizability is fully justified. The organic compounds showing high hyperpolarizability are those containing an electron donating or withdrawing group interacting through conjugated double bonds. Consequently, the present work thought interesting to examine the potential energy surface (PES) at the DFT level of theory in order to obtain the kinetic and thermodynamic parameters as well as reasonable understanding the conversion of “*trans*” and “*ana*” forms in gas phase.

2. Experimental

The mid-IR spectra were recorded in the 4000–400 cm^{-1} region with spectral resolution of 2 cm^{-1} by averaging the results of 16 scans on a Perkin–Elmer RXI Fourier Transform spectrophotometer using KBr pellet technique (solid phase). The ultraviolet absorption spectrum was examined in the range of 200–800 nm using Perkin–Elmer lambda 25 recording spectrophotometer. The photoinduced (*trans*) form was formed upon UV irradiation (Hg lamp DRSh-260+ UV-transmitting glass filters). Cyclic voltammetry measurements were performed by means of AUTOLAB PGSTAT20 potentiostat-galvanostat (EcoChemie, Netherlands). The electrochemical properties of title compound ($c = 2 \times 10^{-3}$ M) was investigated by cyclic voltammetry with CH_2Cl_2 as the solvent in the presence of 0.1 M Bu₄NBF₄ as the supporting electrolyte using Pt working and counter electrodes and Ag/AgCl as reference electrode at ambient temperature [21]. Prior to the measurements the solution was purged with argon to remove residual oxygen. The NMR spectra were recorded for *trans* form at ambient temperature on a Bruker AVANCE DRX 400 MHz using CDCl_3 as solvent. Melting point was measured on a Buchi 510 melting point apparatus and is uncorrected. Chemicals were obtained from Merck and Fluka and used without further purification. The development of reaction was monitored by thin layer chromatography (TLC) analysis on silica gel 60 GF₂₅₄ aluminum sheets, using ethyl acetate:petroleum ether (1:3) as mobile phase. The spots were exposed by UV light and iodine vapor.

2.1. Synthesis of 4-((9,10-dioxo-9,10-dihydroanthracen-1-yl)oxy)benzaldehyde (3) (Scheme 2)

The starting 1-dichloroanthraquinone 1 (2.77 g, 10 mmol) and 4-hydroxybenzaldehyde 2 (2.8 g, 11 mmol) were dissolved in 30 mL of dry *N,N*-dimethylformamide (DMF) in round bottom flask, followed by addition of dry K_2CO_3 (6.9 g, 49.9 mmol) while the solution was stirred at reflux. Stirring was continued for 36 h at reflux conditions. After completion of the reaction, it was monitored by TLC, solvent was evaporated under vacuum and water added to



Scheme 2. Synthesis of 4-((9,10-dioxo-9,10-dihydroanthracen-1-yl)oxy)benzaldehyde (3).

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