Dyes and Pigments 123 (2015) 341–348

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Amino substituted 4-pyridylbutadienes: Synthesis and fluorescence investigations

Harsha Agnihotri [b], Paramasivam Mahalingavelar [b], Hemant Mande [a], Prasanna Ghalsasi [a], Sriram Kanvah [b], *

[a] Department of Chemistry, MS University of Baroda, Pratapgunj, Vadodara, Gujarat 390002, India
[b] Department of Chemistry, Indian Institute of Technology Gandhinagar, Chandkheda, Ahmedabad 382 424, India

ARTICLE INFO

Article history:
Received 4 May 2015
Received in revised form
27 July 2015
Accepted 17 August 2015
Available online 25 August 2015

Keywords:
Solvatochromism
Pyridyl dyes
Donor-acceptor systems
Julolidine
Intramolecular charge transfer
Diarylpolyenes

ABSTRACT

Synthesis and spectroscopic investigations of a series of donor-π-acceptor systems containing pyridine as the electron withdrawing group and an amino derivative (dimethylamino, diphenylamino, carbazole and julolidine) as electron donating group, separated by a π-spacer are described. The effect of varying donors on absorption and emission properties was studied in different solvents. All the molecules investigated exhibit pronounced positive polarity dependent solvatochromic shifts of up to ~141 nm. Strong fluorescence quantum yields are also observed for dienes containing carbazole and diphenylamine donors. This behavior suggests the presence of highly polar emitting states as a result of π -π* intramolecular charge-transfer (ICT). The observations were corroborated by a linear relation of the fluorescence maximum (ν_{max}) versus the solvent polarity function (Δ_f) from the Lippert–Mataga correlation. The emission lifetime shows a decay profile consistent with the formation of one species (**1** and **3**) and two species (**2** and **4**) in the excited state.

1. Introduction

π-conjugated substrates bearing π-electron donor (D) and a π-electron acceptor substitutions exhibiting intramolecular charge transfer (ICT) have gained prominence for use as functional organic materials [1–6]. Among many known substrates, derivatives such as donor-acceptor substituted diphenylpolyenes have attracted attention as model compounds to understand the light induced conformational processes of biological substrates [7] and also as fluorescence probes [8]. Replacement of CH of the phenyl ring of diphenylpolyenes by nitrogen (N) leads to an isoelectronic species that is expected to have significant influence on the electronic properties due to the presence of (n,π*) states [9]. Consequently, neutral styryl and butadienyl pyridine analogs have been synthesized and were investigated for their solution and/or solid state photochemical [10–12] and photophysical properties [13–15]. Examples of photochemical investigations include regioselective photodimerization [16,17], formation of pre-organized molecular ladderane like structures through hydrogen bonding interactions [18] and photoisomerization studies [10,12,14]. Apart from its role towards photochemical transformations, the lone pair of electrons on the nitrogen atom of the pyridine contributes to a coordinate covalent bonding with Lewis acid sites of TiO_2 surface lending its utility as anchoring group for dye-sensitized solar cells applications [19–21]. Because of the facile protonation of pyridine moiety and its role in deactivating effect of the (n, π*) state [22], these substrates have also been utilized as potential fluorescence probes for biological applications [23–28] and also for non-linear optical (NLO) applications [29,30]. In contrast to research investigations on unsubstituted pyridylbutadiene derivatives, the emission properties of the electron donor or acceptor substituted heterocyclic (pyridine) derivatives of butadienes are scarce. Here in, we report synthesis and solvatochromic properties of novel amino [dimethylamino, diphenylamino, carbazole and julolidine] substituted 4-pyridylbutadiene derivatives (Fig. 1). Through this study, we also intend to examine influence of extended π-conjugation on the steady state and time resolved emission properties of the substrates. The results suggest remarkable fluorescence properties characterized by intramolecular charge transfer (ICT).

2. Experimental

The reagents required for the synthesis of pyridyl substituted derivatives were obtained from Sigma–Aldrich, Alfa Aesar, Acros

---

* Corresponding author.
E-mail addresses: kanvah@gatech.edu, sriram@iitgn.ac.in (S. Kanvah).

http://dx.doi.org/10.1016/j.dyepig.2015.08.018
0143-7208/

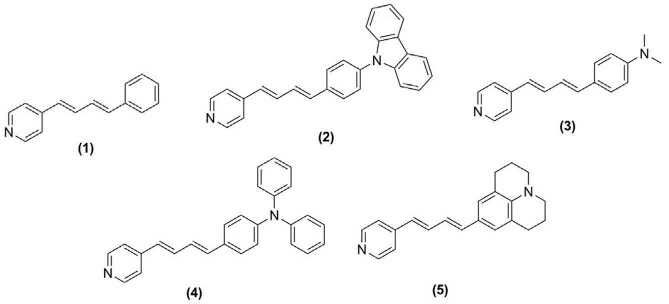

Fig. 1. Structures of synthesized 4-pyridyl-4-phenylbutadiene derivatives.

and S.D. Fine. The solvents utilized for the synthesis and spectral studies were dried using reported procedures. ^1H and ^{13}C NMR spectra were carried out using 500 MHz Bruker Avance spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Accurate mass analysis was performed using Waters-Synapt G2S (ESI-QToF) mass spectrometer. Absorption spectra were recorded on Analytik Jena, Specord 210 model UV–vis spectrophotometer. Steady state fluorescence studies were performed utilizing Horiba Jobin-Yvon fluorolog-3 spectrofluorimeter and relative fluorescence quantum yields were measured using quinine sulfate (0.545 in 0.5 N H_2SO_4) as a standard [31]. The concentrations used for fluorescence experiments are typically in the order of 10^{-5} M. The excitation wavelengths were set at the absorption maxima (λ_a) of the compounds while recording their emission spectra. Fluorescence life-times were determined by Edinburgh Life Spec II instrument at excitation wavelengths of 360 nm for (**2**), 405 nm for (**3**–**5**). The percent error associated with the lifetime studies is 0.1–0.3%.

2.1. X-ray crystallographic details

Crystallographic data for the compound (**4**) was collected on Xcalibur, Gemini with EOS detector diffractometer. The reflection data was integrated and reduced using CrysAlisPro and Superflip [32] and the structure was refined using SHELXS97 [33]. ORTEP diagrams of the compound generated using ORTEP-3. The single crystals of (**4**) were grown in acetone solvent system. The crystallographic data reveal that the compound (**4**) crystallized into a triclinic crystal system with space group P-1 with Z = 2 and shows a *trans*-configuration. Crystallographic data and the ORTEP diagram are given in the supporting information [Tables C1–C3 and Fig. C1].

2.2. Synthesis of (**1**), (**3**), (**4**) and (**5**)

The synthetic scheme for the preparation of dienes (**1**), (**3**–**5**) is given in Scheme 1c. In a typical procedure [15], a mixture of diphenyl (4-picolyl)phosphane oxide [34] (1 equiv), NaH (2.5 equiv), 18-crown-6 (0.5 equiv) was stirred in 40 mL of dry THF at 0 °C. After 30 min of stirring, 4-substituted cinnamaldehyde (1 equiv) in dry THF was added drop wise and allowed to stir for 10 h at room temperature. The reaction mixture was then filtered over celite and the desired product was purified by column chromatography using neutral silica gel using 30% ethyl acetate/petroleum ether.

2.2.1. N,N-dimethyl-4-((1E,3E)-4-(pyridin-4-yl)buta-1,3-dienyl) aniline (**3**)

Brown solid, ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.50 (d, 2H), δ 7.36-7.35 (d, 2H), δ 7.15-7.09 (dd, 1H, J = 15.5 Hz), δ 6.80-6.68 (m, 4H), δ 6.47-6.44 (d, 1H, J = 15.5 Hz), δ 2.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 150.56, 149.89, 136.54, 134.68, 128.03, 126.95, 123.93, 120.42, 112.29, 40.34. HRMS $[M+1]^+$ 251.1550.

2.2.2. N,N-diphenyl-4-((1E,3E)-4-(pyridin-4-yl)buta-1,3-dienyl) aniline (**4**)

Yellow solid, ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.51-8.50 (d, 2H), δ 7.32-7.26 (m, 8H), δ 7.14-7.09 (m, 5H), δ 7.05-7.00 (m, 4H), δ 6.86-6.80 (m, 1H, J = 15.5 Hz), δ 6.73-6.70 (d, 1H, J = 15.5 Hz), δ 6.53-6.49 (d, 1H, J = 15.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 149.96, δ 148.06, δ 147.36, δ 144.9, δ 135.56, δ 134.06, δ 130.58, δ 129.36, δ 128.58, δ 127.65, δ 126.39, δ 124.81, δ 123.39, δ 123.02, 120.54. HRMS [ESI] $[M+1]^+$ 375.1859.

2.2.3. 9-((1E,3E)-4-(pyridin-4-yl)buta-1,3-dienyl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline (**5**)

Brown solid; ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ8.48-8.47 (d, 2H), 7.23-7.22 (2H, d), 7.12-7.07 (m, 1H, J = 15.5 Hz), 6.91 (s, 2H), 6.73-6.68 (m, 1H, J = 15.5 Hz), 6.62-6.59 (d, 1H, J = 15 Hz), 6.42-6.39 (d, 1H, J = 15 Hz), 3.19-3.17 (4H, t), 2.76-2.73(4H, t), 1.97-1.95 (4H, t); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ151.7, 149.8, 145.4, 143.3, 136.9, 134.8, 126.2, 125.8, 124.0, 123.0, 121.2, 120.3, 49.9, 27.7, 21.8 HRMS] $[M+1]^+$ 303.1868.

2.3. Synthesis of 9-(4-((1E,3E)-4-(pyridin-4-yl)buta-1,3-dien-1-yl) phenyl)-9H-carbazole (**2**)

Derivative (**2**) was synthesized by a method [35] showed in Scheme 1d. A mixture of carbazole (60 mg, 0.350 mmol), 4-((1E,3E)-4-(4-bromophenyl)buta-1,3-dienyl) pyridine diene (**13**) (100 mg, 0.350 mmol), CuI (0.0350 mmol), 18-Crown-6 (0.012 mmol), K_2CO_3 (100 mg, 0.7 mmol) and 1 ml of 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) was put into a round bottom flask, and then heated at 170 °C for 13 h under nitrogen atmosphere. After cooling to room temperature, the mixture was quenched with 1 N HCl, and the precipitate was washed with NH_3–H_2O and water. The residue was extracted with ethyl acetate, dried over Na_2SO_4 and then concentrated under vacuum. The reaction mixture was purified on silica-gel column chromatography using 35% ethylacetate/hexane as eluent.

Characterization data: Orange solid ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.57 (m, 2H), δ 8.15-8.14 (d, 2H), δ 7.69-7.67 (d, 2H), δ 7.57-7.56 (d, 2H), 7.46-7.40 (m, 4H), 7.31-7.29 (m, 4H), 7.21-7.16 (m, 1H, J = 15.5 Hz), 7.07-7.02 (m, 1H, J = 15.5 Hz), 6.89-6.85 (d, 1H, J = 15.5 Hz), 6.66-6.62 (d, 1H, J = 15.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.73, 150.21, 144.48, 140.69, 137.49, 135.83, 134.63, 133.34, 130.37, 128.93, 128.03, 127.21, 126.00, 123.51, 120.70, 120.36, 120.11, 109.79. HRMS $[M+1]^+$ 373.1699.

2.4. Computational details

Density functional theory (DFT) calculations have been performed using Gaussian 09 *ab initio* quantum chemical software package. DFT has been used for the ground-state properties and time-dependent DFT (TDDFT) for the estimation of ground to excited-state transitions. The geometry optimization of the molecules obtained using non-local functional B3LYP with 6-31G (d, p) basis set without any symmetry constraints. The minimized geometry was further confirmed by vibrational analysis, resulting in no imaginary frequencies and used as the input for further calculations to obtain the frontier molecular orbitals (FMOs) and single-point TDDFT studies (first 15 vertical singlet–singlet transitions) to obtain the UV–Vis spectra. The integral equation formalism polarizable continuum model (PCM) within the self-consistent reaction field (SCRF) theory, has been used for TDDFT calculations to describe the solvation of the dye in acetonitrile solvent. The