



Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: <http://www.elsevier.com/locate/molstruc>

Experimental and theoretical studies on new 7-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-10-alkyl-10*H*-phenothiazine-3-carbaldehydes

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ARTICLE INFO

Article history:

Received 28 June 2016

Received in revised form

19 October 2016

Accepted 6 November 2016

Available online xxx

Keywords:

Carbazole

Phenothiazine

GIAO

Polarizabilities

Hyperpolarizabilities

ABSTRACT

Synthesis of fused heterocyclic aldehydes with carbazole (CZ) structural motif linked at C-7 position on phenothiazines (PTZ), 7-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-10-butyl-10*H*-phenothiazine-3-carbaldehyde (**1**) and 7-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-10-hexyl-10*H*-phenothiazine-3-carbaldehyde (**2**) has been accomplished and are characterized through experimental and computational techniques. The optimized structure with their bonding aspects and vibrational frequencies of the same have been examined utilizing DFT-B3LYP technique with a basis set 6-311++G(d,p). In the optimized structures of **1** and **2**, the bond lengths and bond angles are in accord with their corresponding reported analogous. The vibrational frequencies resulted from experimental as well as theoretical are in well accord with each other. Further, the results of polarizabilities, first order hyperpolarizabilities and dipole moment of **1** and **2** imply that these could be utilized for the preparation of NLO crystals which might generate second order harmonic waves.

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1. Introduction

Carbazole (CZ), also branded as 9-azafluorene, and its derivatives are incredibly significant nitrogen possessing hetero-aromatic compounds, which have been used as potential building blocks in the construction of a wide range of functional materials [1]. Besides, the CZ structural scaffold has been found in several bio-important chemical entities and exhibit antifungal [2], antibacterial [3], anti-inflammatory [4], antiviral [5], and antitumor properties [6]. Alkyl functionalized carbazoles play noteworthy roles in electron transport materials/dye-sensitized solar cells. For instance, it is known that CZ is an electron donor because of the existence of lone pair of electrons on the nitrogen. Since alkyl groups are electron donors in nature through inductive effect, incorporation of such groups on the CZ structural motif enhances the electron donating ability of the CZ unit. Further, introduction of alkyl groups helps in enhancing the materials solubility as well.

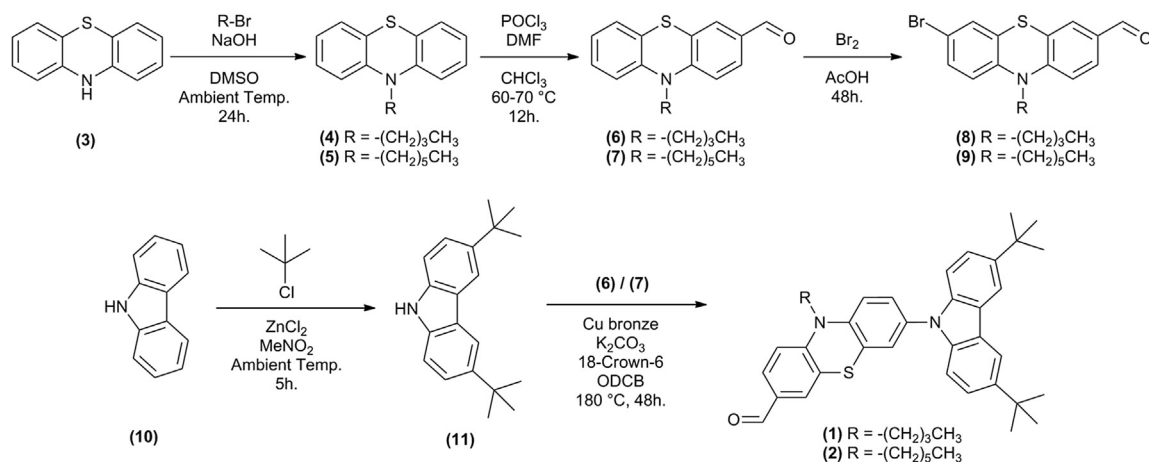
Phenothiazine (PTZ) and its derivatives are one of the classes of outstanding heterocyclic compounds with excellent electron donating nature and hence these trigger researchers to focus their

attention towards electro-chemical [7] and electro-optical properties [8]. They are widely used as potential intermediates in chemical manufacturing and active components of organic light emitting diodes (OLEDs) [9], semiconductors [10] and solar cells [11]. Besides their potential applications in materials science, PTZ has been utilized to construct chemical entities of biological significance which display various activities including anti-malarial [12], anti-cancer [13], anti-helminthic [14], anti-histamine [15] and anti-psychotic activity [16].

The wide variety of applications of organic molecules possessing CZ and PTZ structural motifs reported in the literature inspired us to focus our attention towards new systems carrying these two carbazole-phenothiazine moieties. We herein report synthesis as well as experimental and computational studies on compounds **1** and **2**. Structural parameters (optimized) were obtained by the calculations of density functional theory (DFT) with a basis set B3LYP/6-311++G(d,p). From the theoretical results, vibrational assignments and optimized structural parameters are deduced and these outcomes are correlated with the experimental results. The theoretical outcomes are found to be appreciably comparable with the experimental results.

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Scheme 1. Synthesis of 7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-10-alkyl-10H-phenothiazine-3-carbaldehydes.

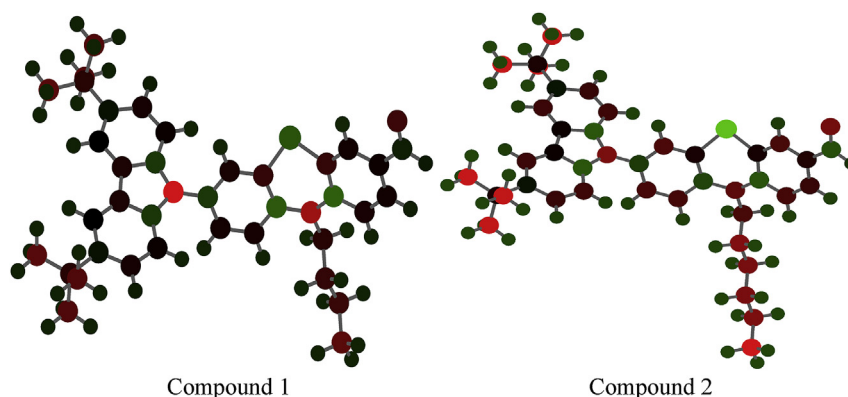


Fig. 1. Optimized structure and Mulliken charge distribution indicated by color code of compounds 1 and 2.

2. Experimental section

2.1. Characterization

The melting point of the title heterocyclic carbaldehydes was measured in capillaries (open) and is un-corrected. IR spectra of the synthesized molecules were acquired on Shimadzu IR Tracer-100 in the range between 400 and 4000 cm^{-1} utilizing KBr pellet form (resolution – 04; number of scans – 25). The spectral assignments are reported in wavenumber (cm^{-1}). Spectra of ^1H and ^{13}C NMR were obtained on Bruker spectrometer (400 MHz) using chloroform-D (CDCl_3) as a solvent. The values of chemical shifts are given in parts per million (ppm) from tetramethylsilane (TMS). UV–Vis spectra of the molecules have been obtained in dichloromethane (DCM), hexane, and ethanol in the region 200–800 nm and the spectrophotometer used for the same is JASCO V-650.

2.2. Synthesis of heterocyclic carbaldehydes 1 and 2

2.2.1. Synthesis of intermediates

The intermediates, alkylphenothiazines 4 and 5, alkylphenothiazine carbaldehydes 6 and 7, bromophenothiazine carbaldehydes 8 and 9, and alkylcarbazole 11 were synthesized by employing literature methods [17–19].

2.2.2. Synthesis of heterocyclic carbaldehyde 1

In a double neck round-bottomed flask (100 mL) with water

condenser under nitrogen atmosphere, was charged bromophenothiazine carbaldehyde 8 (0.50 g, 1.38 mmol), alkylcarbazole 11 (0.39 g, 1.38 mmol), potassium carbonate (0.6 g, 4.34 mmol), copper-bronze (0.14 g, 2.16 mmol), and 18-crown-6 (0.06 g, 0.20 mmol). Then, 1,2-Dichlorobenzene (20 mL) was added using a syringe and stirred for two minutes. It was then heated to reflux and continued the same with stirring for 48 h. After cooling, it was filtered and the dark-brown filtrate-solution was collected. The insoluble material was rinsed with dichloromethane (3×30 mL). The rinsed solution thus obtained together with the collected dark-brown filtrate was washed with a dilute solution of aqueous ammonia followed by water. The washed dichloromethane, after drying over anhydrous magnesium sulfate, was evaporated with the help of rotary evaporator to provide a crude mixture. The pure title compound was eventually obtained upon column chromatographic separation using hexane-dichloromethane mixture (4:6). Yield: 0.56 g (73%), mp. 218–220 $^\circ\text{C}$. IR (KBr, cm^{-1}): 3055–2713 (C–H aromatic & aliphatic), 1693 (C=O aldehyde), 1602, 1579 (C=C), 1257, 1236 (C–N), 1101 (C–S); ^1H NMR (400 MHz, CDCl_3): δ 9.82 (s, 1H), 8.12 (d, $J = 1.20$ Hz, 2H), 7.70–7.68 (m, 1H), 7.62 (s, 1H), 7.47–7.44 (m, 2H), 7.34–7.26 (m, 4H), 7.04 (d, $J = 6.00$ Hz, 1H), 6.97 (d, $J = 8.40$ Hz, 1H), 3.97 (t, $J = 7.20$ Hz, 2H), 1.92–1.85 (m, 2H), 1.63–1.52 (m, 2H), 1.45 (s, 18H), 1.01 (t, $J = 7.40$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3): δ 190.00, 150.39, 142.94, 142.34, 139.25, 133.81, 131.31, 130.24, 128.65, 125.88, 125.69, 125.36, 124.50, 123.65, 123.30, 116.59, 116.29, 115.03, 109.12, 47.99, 34.77, 32.04, 29.74, 20.18, 13.84; Anal. Calcd for $\text{C}_{37}\text{H}_{40}\text{N}_2\text{O}$: C, 79.24; H, 7.19; N, 5.00; S, 5.72. Found:

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