

Synthesis and Characterization of Pyrano[3,2-C]Chromene Derivatives: Exploring Their Optoelectronic and Charge Transport Properties by First-Principles Approach

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ABSTRACT: With the aim to enhance the charge transport, optoelectronic and semiconducting properties various multifunctional pyrano[3,2-c]chromene derivatives were synthesized and characterized. To shed light on the various properties of interests, the ground state geometries were optimized by Density Functional Theory (DFT). The effect of different substituents, e.g., thiophen-2-yl, 5-bromothiophen-2-yl, 1H-indol-3-yl, pyridin-3-yl, and benzo[d][1,3]dioxol-5-yl was studied on the structural stability, electronic properties, and absorption wavelengths by DFT and Time-Domain DFT (TDDFT). The experimental excitation energies were successfully reproduced at TD-PBE/6-31G** level in DMSO. The electron injection barrier, ionization potential, electron affinity, and reorganization energies for hole and electron were calculated and compared systematically. The smaller electron reorganization energies of pyrano[3,2-c]chromene derivatives except indole substituted one is illuminating that these materials would be efficient to be used in n-type semiconductor devices.

KEYWORDS: Organic semiconductors; Pyrano[3,2-c]chromene derivatives; Synthesis; Density functional theory; Charge transport; Optoelectronic properties.

INTRODUCTION

Recent researches in the development of organic semiconducting materials have witnessed tremendous growth in the area of organic electronics that include Organic Light-Emitting Diodes (OLEDs), Organic Field-Effect Transistors (OFETs), electrochromic and photovoltaic devices [1-5]. Organic-based photovoltaic

materials have the advantage over inorganic based counterpart due to their flexible shape, lightweight, versatile technological process, economic at large-scale industrial production, ease of modifying the chemical structure, optimizing their structural, electrical, and optical properties [6].

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Organic materials having N-heterocyclic moiety are extensively used to construct optoelectronic materials such as OLEDs, Dye-Sensitized Solar Cells (DSSCs), organic and heterojunction solar cells [7-9]. However, among many organic compounds, pyrazoles appended molecular materials have received great attention for the fabrication of photovoltaic and photorefractive materials owing to their specific photophysical properties such as low ground state dipole moments which favor enhancing the photovoltaic performance [10]. The electron-rich pyrazole unit performs well as a donor-acceptor type of functional material due to strongly electron-donating nature, better hole transfer and photoelectron ability [11]. Hence, pyrazole derivatives have widely been used as hole transport materials in DSSCs and the OLEDs. Previously, pyrano[3,2-c]chromene derivative was synthesized and various functional properties were probed by advanced quantum chemical techniques [12]. Pawar et al., described synthetic microwave procedure of pyrano[3,2-c]chromene derivative was catalyzed by Cesium Carbonate [13].

Multi-component reactions for the synthesis of pyrano[3,2-c]chromenes from different aromatic aldehydes with a mixture of malononitrile and 4-hydroxycoumarin were established. The chemistry of chromenes has attracted the interest of many areas due to their applications such as red fluorescent emitters [14, 15], Pyran derivatives have been used widely in electroluminescent devices due to their fluorescent properties [16], Chromenopyrazoles are being used in thermally activated delayed fluorescence OLEDs [17].

To unravel the relationship between chemical structures and charge transport properties, we have synthesized 2-amino-4-(heteryl)-5-oxo-4*H*,5*H*-pyrano[3,2-c]chromene derivatives, *i.e.*, 2-amino-5-oxo-4-(thiophen-2-yl)-4*H*,5*H*-pyrano[3,2-c]chromene-3-carbonitrile (**4a**), 2-amino-4-(5-bromothiophen-2-yl)-5-oxo-4*H*,5*H*-pyrano[3,2-c]chromene-3-carbonitrile (**4b**), 2-amino-4-(1*H*-indol-3-yl)-5-oxo-4*H*,5*H*-pyrano[3,2-c]chromene-3-carbonitrile (**4c**), 2-amino-5-oxo-4-(pyridin-3-yl)-4*H*,5*H*-pyrano[3,2-c]chromene-3-carbonitrile (**4d**), and 2-amino-4-(benzo[d][1,3]dioxol-5-yl)-5-oxo-4*H*,5*H*-pyrano[3,2-c]chromene-3-carbonitrile (**4e**), see Scheme 1. The effect of various substituents on the optoelectronic properties, charge transport and electron injection was systematically studied to explore new types of optoelectronic and semiconductor materials.

EXPERIMENTAL SECTION

Experimental Details

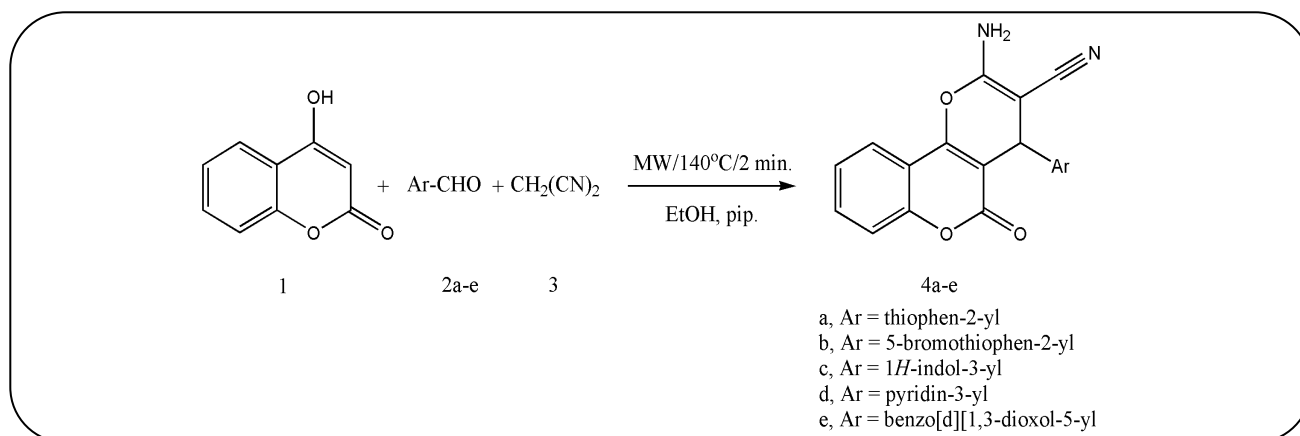
All chemicals were purchased from Sigma-Aldrich Chemical Co. Melting points were determined with a Stuart Scientific Co. Ltd apparatus and are uncorrected. IR spectra were determined as KBr pellets on a Jasco FT/IR 460 plus spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded using a BRUKER AV 500/600 MHz spectrometer. The microwave apparatus used is Milestone Sr1, Microsynth. The MS were measured on a Shimadzu GC/MS-QP5 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 microanalyser and all compounds are within ±0.3% of theory specified. Previously, through Knoevenagel reaction between aldehyde and malononitrile in presence of cesium carbonate to form adduct I. Finally, various dihydropyrano[3,2-c]chromenes were synthesized [13]. In present work, through Knoevenagel reaction between aldehyde and malononitrile in presence of piperidine we have synthesized 2-amino-4-(heteryl)-5-oxo-4*H*,5*H*-pyrano[3,2-c]chromene derivatives using piperidine as catalyst under microwave irradiation conditions to improve the yield and reduce the reaction time.

General procedure for the synthesis of 2-amino-4-(heteryl)-5-oxo-4*H*,5*H*-pyrano[3,2-c]chromene derivatives

4-Hydroxycoumarin **1** (0.01 mol), hetero aromatic aldehyde **2a-e** (0.01 mol) and malononitrile **3** (0.01 mol) in 30 mL ethanol and 0.5 ml of piperidine was exposed to pulsed microwave irradiation for 2 min at 140°C. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature and the separated solid was filtered and recrystallized from ethanol. The physical data for **4a - 4e** are as follows:

2-Amino-5-oxo-4-(thiophen-2-yl)-4*H*,5*H*-pyrano[3,2-c]chromene-3-carbonitrile (**4a**)

White crystals, (ethanol), yield 78 %, mp 267-269°C, IR (KBr, ν max cm^{-1}), 3367, 3279, 3174 (NH_2), 2200 (CN), 1709 (C=O), 1636 (C=C); ¹H NMR (DMSO-*d*₆, 500 MHz) δ : 7.38-7.87 (m, 4 H, aromatic), 7.44 (s, 2H, , NH_2), 7.38 (d, C-5, thiophene), 7.03 (t, C-4, thiophene), 6.95 (d, C-3, thiophene), 4.82 (s, H-4); ¹³C NMR (DMSO-*d*₆, 125 MHz), 159.42 (C=O), 158.39 (C-2), 152.98, 152.03, 147.43, 133.05 (C-2, thiophene), 127.04 (C-4, thiophene), 125.49 (C-5, thiophene), 125.17, 124.70 (C-3 thiophene), 122.41,



Scheme 1: Synthesis 2-amino-4-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene derivatives (4a-4e).

119.05, 116.56, 112.77, 104.01, 57.83 (C-3), 32.06 (C-4), Anal. Calcd for C₁₇H₁₀N₂O₃S: C, 63.35; H, 3.13; N 8.69. Found C, 6.13; H, 2.95; N, 8.49.

2-Amino-4-(5-bromothiophen-2-yl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile (4b)

Pale yellow crystals (ethanol), yield 89 %, mp 269-271°C, IR (KBr, ν max cm⁻¹), 3363, 3251, 3192 (NH₂), 2209 (CN), 1708 (C=O), 1667 (C=C); ¹H NMR (DMSO-d₆, 500 MHz), 7.44-7.86 (m, 4 H, aromatic), 7.46 (s, 2H, NH₂), 7.06 (d, H-3 thiophene), 6.87 (d, H-4, thiophene), 4.78 (s, H-4); ¹³C NMR (d, CH, (DMSO-d₆, 125 MHz), 160.06 (C=O), 159.08 (C-2), 153.78, 152.69, 149.67, 133.82 (C-2, thiophene), 130.91 (C-4, thiophene), 126.81 (C-5, thiophene), 125.39, 122.98, 119.47, 117.28, 113.34, 110.76, 103.80, 57.43, 33.02 (C-4); Anal. Calcd for C₁₇H₉BrN₂O₃S: C, 50.89; H, 2.26; N, 6.98. Found: C, 50.66; H, 2.05; N, 6.79.

2-Amino-4-(1*H*-indol-3-yl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile (4c)

Yellow crystals (ethanol), yield 84 %, mp 245-246°C, IR (KBr, ν max cm⁻¹), 3424, 3322, 3184 (NH₂), 2188 (CN), 1690 (C=O), 1654 (C=C); ¹H NMR (DMSO-d₆, 500 MHz), 11.02 (NH, indole), 7.31-7.43 (m, 9 H, aromatic), 7.38 (s, 2H, NH₂), 4.76 (s, H-4); ¹³C NMR (DMSO-d₆, 125 MHz), 160.08 (C=O), 158.68 (C-2), 153.33, 152.57, 137.17, 133.27, 125.21, 124.70, 122.95, 121.51, 119.31, 118.44, 117.09, 116.51, 112.45, 104.73, 58.80, 29.35 (C-4); Anal. Calcd for C₂₁H₁₃N₃O₃: C, 70.98; H, 3.69; N, 11.83. Found: 7.77; H, 3.67; N, 11.61.

2-Amino-5-oxo-4-(pyridin-3-yl)-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile (4d)

White crystals (ethanol), yield 92 %, mp 263-265°C, IR (KBr, ν max cm⁻¹), 3365, 3282, 3177 (NH₂), 2202 (CN), 1706 (C=O), 1637 (C=C); ¹H NMR (DMSO-d₆, 500 MHz), 8.46 (d, H-5, pyridine), 8.56 (s, H-2, pyridine), 7.34-7.90 (m, 6 H, aromatic), 7.71 (2H, NH₂), 4.55 (s, H-4); ¹³C NMR (DMSO-d₆, 125 MHz), 159.53 (C=O), 158.06 (C-2), 153.78, 152.19, 149.03 (C-2, pyridine), 148.23, 147.89 (C-5, pyridine), 135.45 (C-4, pyridine), 132.96 (C-3, pyridine), 124.60, 123.78, 122.52, 119.01, 116.51, 112.90, 102.91, 57.04, 34.69 (C-4); Anal. Calcd for C₁₈H₁₁N₃O₃: C, 68.14; H, 3.49; N, 13.24. Found: C, 67.49; H, 3.26; N, 13.02.

2-Amino-4-(benzo[d][1,3]dioxol-5-yl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile (4e)

Yellow crystals (ethanol), yield 96 %, mp 265-266°C, IR (KBr, ν max cm⁻¹), 3399, 3317, 1389 (NH₂), 2190 (CN), 1702 (C=O), 1639 (C=C); ¹H NMR (DMSO-d₆, 500 MHz), 7.37-7.90 (m, 7 H, aromatic), 7.42 (s, 2 H, NH₂), 5.97 (dd, CH₂), 4.39 (s, H-4); ¹³C NMR (DMSO-d₆, 125 MHz), 159.50 (C=O), 157.88, 153.26, 152.94, 152.09, 147.30, 146.27, 137.38, 132.78, 124.53, 122.47, 120.94, 119.19, 116.46, 113, 107.62, 103.92, 100.97, 58.15, 36.77 (C-4); Anal. Calcd for C₂₀H₁₂N₂O₅: C, 66.76; H, 3.36; N, 7.77. Found: C, 66.52; H, 3.16; N, 7.58.

Computational Details

Previously, it has been shown that Density Functional Theory (DFT) functionals best reproduce the geometries [18-36]. B3LYP functional [37-39] and 6-31G** basis set [40, 41]

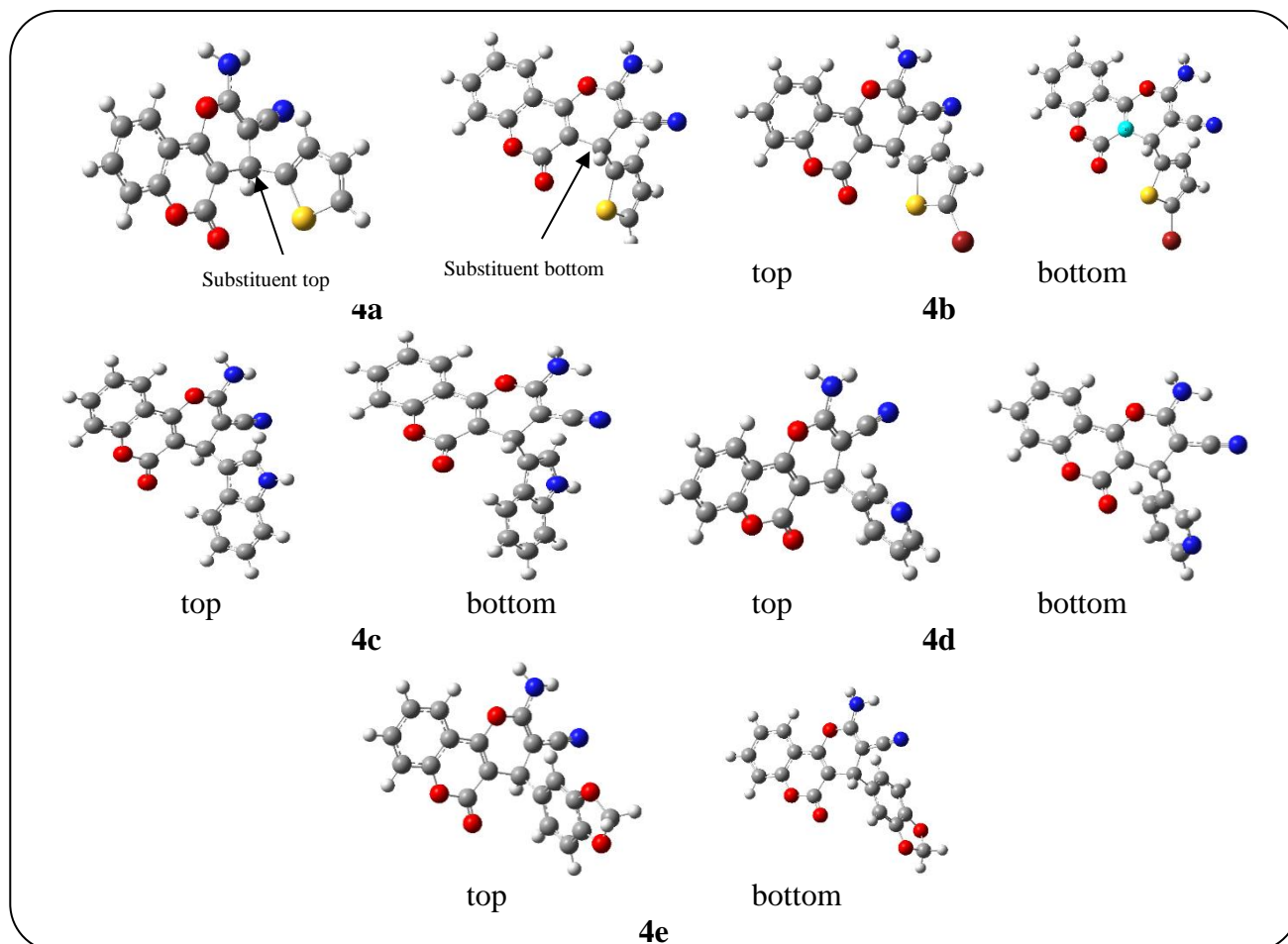


Fig. 1: Optimized top and bottom structures of pyrano[3,2-c]chromene derivatives.

were successfully used for structural, electronic, photophysical and charge transport properties exploration. Some other studies exposed that B3LYP/6-31G** level is a sound method for λ calculation to reproduce experimental data [18, 42, 43]. Here, geometries for ground (S_0) and excited (S_1) states at B3LYP/6-31G** and TDDFT [44, 45] B3LYP/6-31G** levels were optimized, respectively. Moreover, B3LYP/6-31G** level was adopted for ionization potential ($IP_{v/a}$), electron affinity ($EA_{a/v}$) and reorganization energy (λ) (see supporting information for details).

Previously, optical properties were calculated by generalized gradient approximation (GGA) functional, *i.e.*, PBE [46-52] which magnificently reproduced the experimental data [24, 25, 51, 53-56]. The time domain DFT (TD-DFT) was used for absorption spectra calculations [24, 25]. Heretofore, the absorption spectra (λ_{abs}) of pyrazole derivatives was computed by PBE, B3LYP, PBE0, CAM-B3LYP, LCY-PBE and CAMY-

B3LYP functionals. Among different functionals PBE was found the best one to reproduce the experimental data [57]. In current work, TD-PBE [58] along with 6-31G** basis set [40, 41] was adopted for the λ_{abs} insolvant (DMSO) using Polarizable Continuum Model (PCM) [59]. All the quantum chemical calculations were executed by Gaussian16 software [60].

RESULTS AND DISCUSSION

Structures stability

When thiophene, bromothiophene and other substituents were introduced at top (Fig. 1) result more stability than those compounds in which substituents were at bottom, see Table 1.

Electronic properties

The computed energies for highest occupied molecular orbital (HOMO) (E_{HOMO}), lowest unoccupied molecular orbital (LUMO) (E_{LUMO}), HOMO-LUMO energy gaps (E_g)

Table 1: Total and energy differences for top and bottom substituted positions of various pyrano[3,2-c]chromene derivatives computed at B3LYP/6-31G level.**

Compounds	Total energy	Total energy	Difference KJ/mol
	Bottom	Top	
4a	-1387.1833051	-1387.1842306	2.43
4b	-3958.2811777	-3958.2820898	2.39
4c	-1198.0047983	-1198.0060051	3.17
4d	-1082.4675168	-1082.4689855	3.86
4e	-1254.9611285	-1254.9620473	2.41

Table 2: HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO-LUMO energy gap (E_{gap}), absorption wavelengths (λ_{abs}), major transition, % contribution (%Cont.) and oscillator strength (f) of pyrano[3,2-c]chromene derivatives computed at TD-PBE/6-31G in solvent (DMSO).**

Compounds	E_{HOMO}	E_{LUMO}	E_{gap}	f	λ_{abs}	% Transition	%Cont.	λ_{abs}^a
4a	-6.11	-2.08	4.03	0.0953	307	H-4 to L	64	310
4b	-6.04	-2.19	3.85	0.1055	327	H-2 to L	52	330
4c	-5.35	-1.93	3.42	0.0812	322	H-3 to L	70	325
4d	-6.27	-2.15	4.12	0.0117	332	H-1 to L	51	325
4e	-5.56	-2.01	3.55	0.0262	326	H-3 to L	50	325

^a Experimental absorption data in DMSO

in eV of parent compound (**4a**) and its derivatives (**4b** – **4e**) at the S_0 and S_1 are tabulated in Table 2. The E_{HOMO} and E_{LUMO} of the **4c** is higher than other counterparts. The trend in E_{HOMO} is as **4c** > **4e** > **4b** > **4d** > **4a** at the S_0 . The trend in E_{LUMO} owing to substituting strength is as **4c** > **4d** > **4e** > **4a** > **4b** at the S_0 . The trend in the energy gap was found as **4d** > **4a** > **4b** > **4e** > **4c**. The smaller E_g is approaching that **4c** would tune the optoelectronic nature successfully.

The E_{HOMO} is -6.11 eV for **4a** and Aluminum (Al) work function is -4.26 eV, the hole injection energy (HIE) is 1.85 eV ($= -4.26 - (-6.11)$) from **4a** to Al electrode. Hence, the E_{HOMO} level should be bigger in order to increase hole injection aptitude. The computed HIE of are: **4b** (1.78), **4c** (1.09), **4d** (1.81), and **4e** (1.30) eV. The E_{LUMO} level of **4a** is -2.08 eV (see Table 2), the electron injection energy (EIE) from **4a** to Al electrode is 2.18 eV ($= -2.08 - (-4.26)$). The electron injection ability can be increased by lowering the E_{LUMO} level. The computed electron injection barrier is: **4b** (2.07), **4c** (2.33), **4d** (2.31), and **4e** (2.25) eV. The HOMOs and LUMOs charge density for S_0 is illustrated in Figs. 2 and 3 that is revealing comprehensible Intra-molecular Charge Transfer (ICT).

Optical properties

Experimentally electronic absorption spectra of all the studied compounds have been recorded in DMSO. For better comparison purposes computationally absorption spectra were also calculated in DMSO at PBE/6-31G** level and tabulated in Table 2. The computed data at TD-PBE/6-31G** level is in good agreement with available experimental data. Red shift in the computed data for **4b**, **4c**, **4d** and **4e** has been observed 20, 15, 25, and 19 nm as compared to the **4a**. Red shift in the experimental data for **4b**, **4c**, **4d** and **4e** has been observed 20, 15, 15, and 15 nm as compared to the **4a**. We have also studied the natural transition orbitals (NTOs) [61] of all the derivatives which are presented in Fig. 4 developed from TD-PBE/6-31G** level of theory.

Charge transfer

Charge transfer performance can be predicted by IP and EA which can be estimated by DFT to understand the energy barriers for hole and electron injection. Previous studies revealed that smaller IP would be good for hole transfer [62] whereas larger EA for good electron ones.

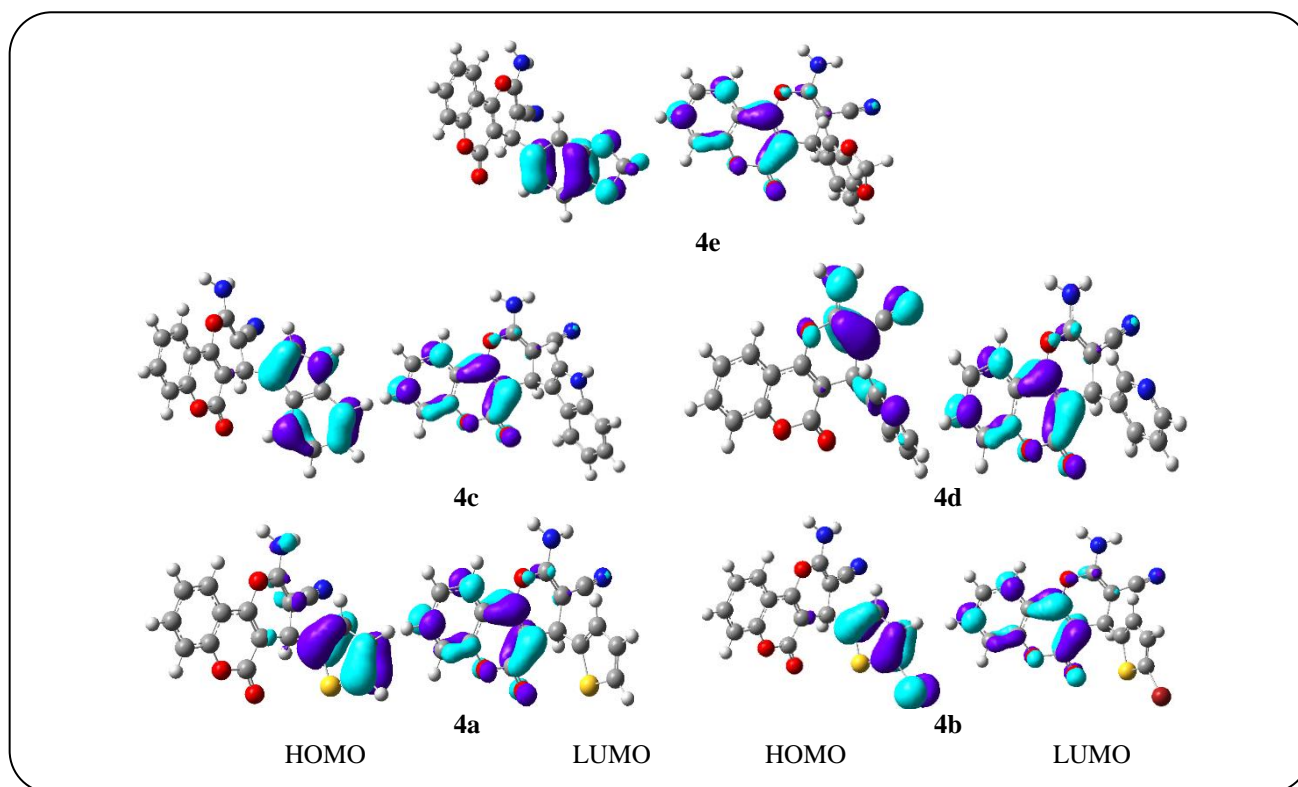


Fig. 2: Ground state HOMOs and LUMOs of the pyrano[3,2-c]chromene derivatives (Contour Value 0.05).

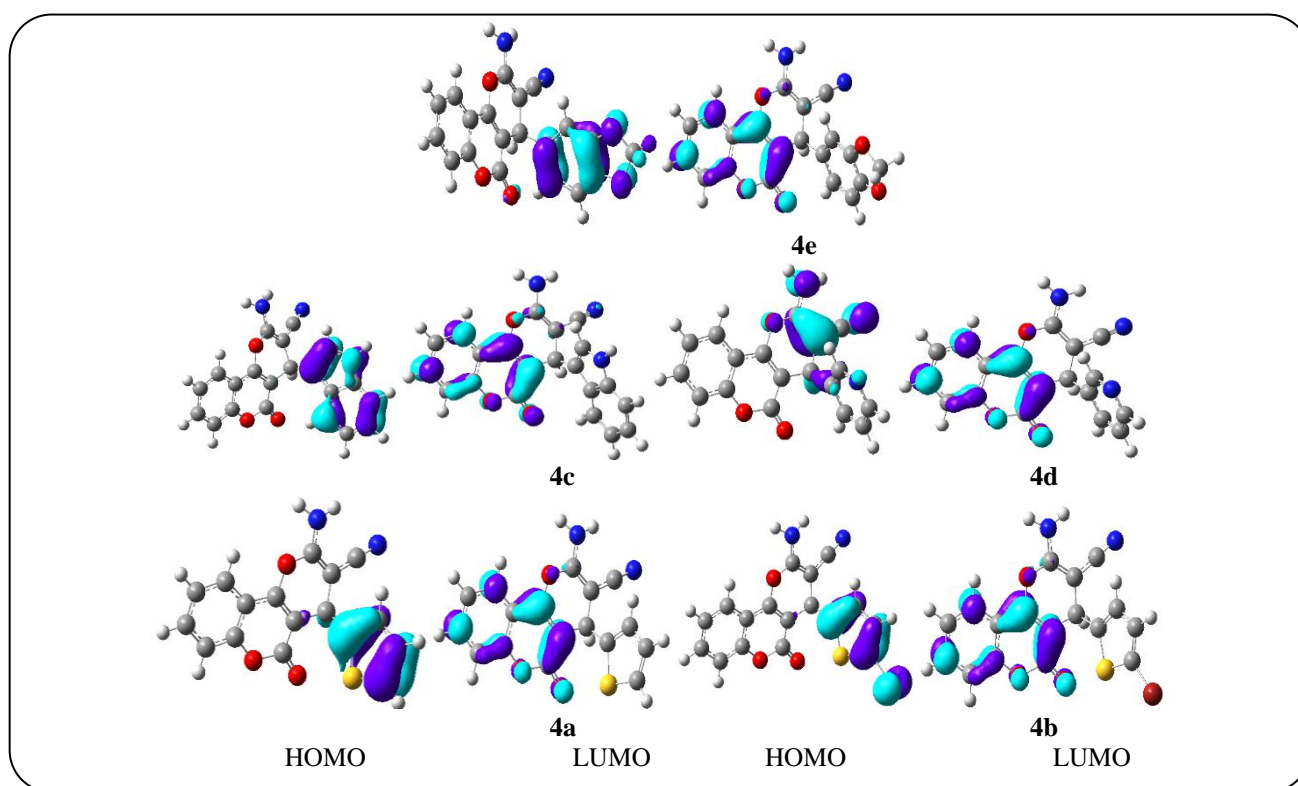


Fig. 3: Excited state HOMOs and LUMOs of pyrano[3,2-c]chromene derivatives (Contour Value 0.05).

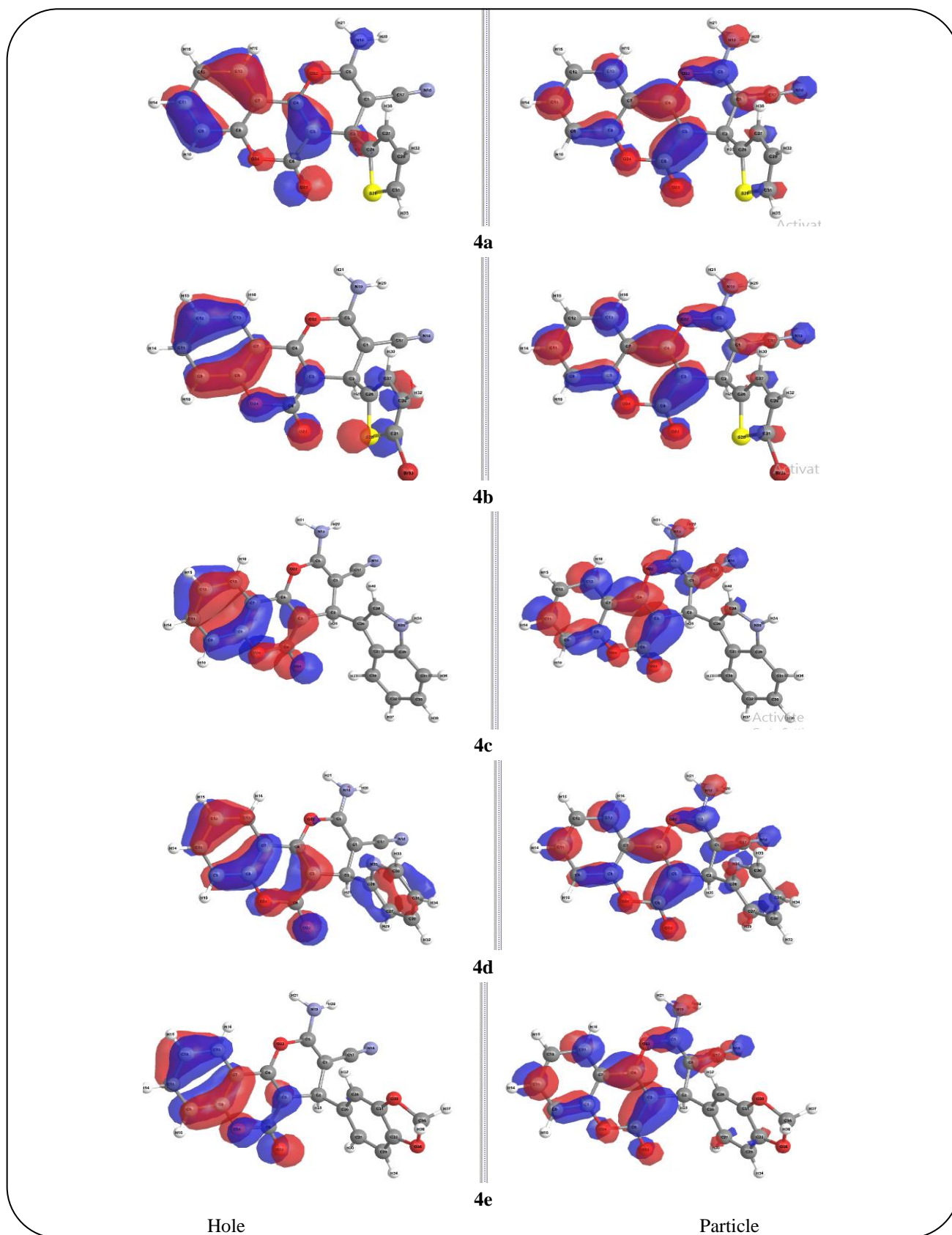


Fig. 4: Occupied (hole, left) and unoccupied (particle, right) NTOs of pyrano[3,2-c]chromene derivatives (isosurface value=0.035).

Table 3: The vertical and adiabatic ionization potentials (IP_v/IP_a), electronic affinities (EA_v/EA_a), hole/electron reorganization energies ($\lambda(h)$ / ($\lambda(e)$) (in eV) at the B3LYP/6-31G level.**

Compounds	IP _a	EA _a	IP _v	EA _v	$\lambda(h)$	$\lambda(e)$
4a	7.353	0.763	7.676	1.016	0.634	0.451
4b	7.321	0.897	7.607	1.276	0.574	0.453
4c	6.755	0.662	6.942	1.396	0.403	0.516
4d	7.393	0.671	7.722	1.559	0.789	0.465
4e	6.983	0.725	7.239	1.757	0.524	0.458

The calculated adiabatic IP (IP_a), vertical IP (IP_v), adiabatic EA (EA_a), and vertical EA (EA_v) are presented in Table 3. The tendency in IP_a is as **4d** > **4b** > **4a** > **4e** > **4c**. The tendency in IP_v is as **4d** > **4a** > **4b** > **4e** > **4c**. The smallest IP_a and IP_v were found for the **4c** illuminating that this compound would be better hole transfer contender than those of other counterparts. The trend in EA_a is as **4b** > **4a** > **4e** > **4d** > **4c** which is revealing that **4b** and **4a** would be better electron transfer materials. By introducing the indole as –R group elevate the IP_a/IP_v of **4c** while diminish the EA_a value.

It is accepted that smaller electron reorganization energy values ($\lambda(e)$) than the hole ones ($\lambda(h)$) would lead to improving the electron transferability of the material which revealed that such materials would be efficient to be used in semiconductor devices as *n*-type. For **4a**, **4b**, **4d**, and **4e**, $\lambda(e)$ values are smaller than those of the $\lambda(h)$ enlightening that prior compound might be good *n*-type materials except **4c**.

CONCLUSIONS

The substitution of various –R groups on top side position is more favorable than the bottom one. The computed and experimental absorption spectra of pyrano[3,2-*c*]chromene derivatives was found in good agreement at TD-PBE/6-31G** level. The calculated electron injection barrier is as **4a** (2.18), **4b** (2.07), **4c** (2.33), **4d** (2.31), and **4e** (2.25) eV. Comprehensible ICT was found from occupied to unoccupied molecular orbitals. The indole substitution (**4c**) leads to higher HOMO level, reduced energy gap, smaller IP, lesser hole reorganization energy resulting better hole transfer candidate to be used in *p*-type semiconductors. The thiophene, bromothiophene, pyridine, and benzo[d][1,3]dioxol reduce the electron reorganization energy resulting better electron transfer contenders to be used in *n*-type

semiconductors. These first-principles investigations showed that pyrano[3,2-*c*]chromene compounds would be efficient charge transfer materials to be applied for versatile activities in various semiconductor devices.

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