

Effect of Donor-Acceptor Chromophores on Photophysical Properties of Newly Synthesized Pyrazolo-Pyrrolo-Pyrimidines (PPP)

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Abstract Novel pyrazolo-pyrrolo-pyrimidine (PPP) derivatives having remarkable photophysical properties are designed with the help of theoretical semiempirical calculations. These compounds then synthesized successfully and studied effect of substituents on its photophysical properties.

Keywords Pyrazolo-pyrrolo-pyrimidine (PPP) ·
Cyclic β -ketoester · HOMO · LUMO · UV · Fluorescence ·
Quantum yield

Introduction

Heterocyclic compounds which absorb in the near visible region and emits lights in the visible region (400–550 nm) are considered to be fluorophores and can be used as organic light emitting diodes (OLEDs). Fluorescent compounds are widely used as markers in biochemical and nucleic acid technologies and is the subject of intensive investigations [1]. There are numbers of efficient blue dyes developed in the past several years [2–8], some of which possess reasonable or high glass transition temperature [T_g], a property suggested to be desirable for morphological stability reasons [9–11]. It was also noted that the heterocyclic compound which are used as light emitting diodes must have electron hole gap between 2.7 to 3 eV and fluoresces between 400 to 700 nm [12]. Photoinduced intramolecular electron transfer plays a key

role in the photophysics of electron donor-accepter π / π conjugated system. The absorption and emission spectra in such case significantly depends on the type of substituents [13, 14]. The heterocycles with high extinction coefficient, large Stoke's shift and quantum yield are near to unity are fluorescent brighteners and these three parameters largely determine both color strength and brightness [15]. Thus, a suitable blue-emitting material with high brightness, low hole gap, high quantum yields and good thermal stability still remain to be developed.

In our earlier communication, synthesis of highly fluorescent dipyrazolo[3,4-*b*:3,4-*d*]pyridines (DPP) [16], pyrazolo[3,4-*b*]pyrrolo[2,3-*d*]pyridines (PPP) [17] and 2,6-dirayl-4-alkoxy pyridine-3-carbonitriles [18] has been reported. These literature reports and our ongoing interest in this area prompted us to extend our study in which new class of heterocycles are synthesized. As theoretically predicted empirical calculations, HOMO-LUMO, electron hole gap, ionization potential and heat of formation helps chemist to design the synthesis of new heterocycles. In the present communication, we design the synthesis of novel pyrazolo-pyrrolo-pyrimidine (PPP) derivatives and studied the effect of substituents on their photophysical properties.

Result and Discussion

Semiempirical Study

As a keen interest, atomic contribution on frontier orbital, we analyzed the three-dimensional HOMO and LUMO coefficient contribution by the MOPAC-2009 (Version 8.331) [19, 20] and are given in Table 1. From empirical calculations it is noted that all derivatives of PPP have

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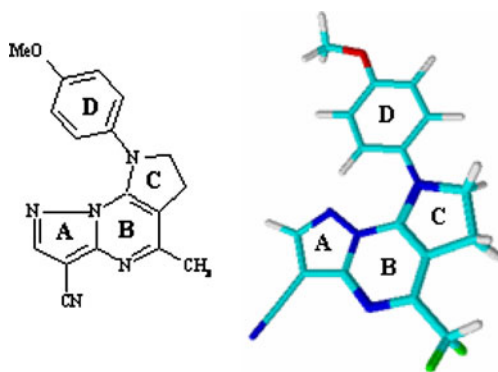
Table 1 The molecular electronic properties (HOMO-LUMO energy GAP) of the Compounds **3**, **4** and **6a–l** at 25 °C

| Comp. | Ar | Heat of formation (K Cal.) | Ionization potential (eV) | HOMO(eV) | LUMO (eV) | GAP ^a (eV) |
|-----------|---|----------------------------|---------------------------|----------|-----------|-----------------------|
| 3 | – | 80.03 | 9.786 | –9.787 | –1.699 | 8.08 |
| 4 | – | 68.07 | 9.256 | –9.257 | –1.105 | 8.15 |
| 6a | p-OCH ₃ -C ₆ H ₄ | 93.28 | 8.686 | –8.686 | –0.855 | 7.83 |
| 6b | p-CH ₃ -C ₆ H ₄ | 124.07 | 8.689 | –8.690 | –0.859 | 7.83 |
| 6c | p-F-C ₆ H ₄ | 86.86 | 8.872 | –8.873 | –1.089 | 7.78 |
| 6d | m-Br-C ₆ H ₄ | 137.06 | 8.887 | –8.887 | –1.082 | 7.80 |
| 6e | P-Br-C ₆ H ₄ | 136.69 | 8.901 | –8.901 | –1.120 | 7.78 |
| 6f | -C ₆ H ₅ | 134.12 | 8.750 | –8.751 | –0.932 | 7.81 |
| 6g | p-NO ₂ -C ₆ H ₄ | 129.49 | 9.218 | –9.218 | –1.802 | 7.41 |
| 6h | m-CH ₃ -C ₆ H ₄ | 123.66 | 8.687 | –8.687 | –0.890 | 7.79 |
| 6i | m-F-C ₆ H ₄ | 86.35 | 8.909 | –8.909 | –1.145 | 7.76 |
| 6j | m-Cl-C ₆ H ₄ | 124.90 | 8.879 | –8.880 | –1.083 | 7.79 |
| 6k | o-CH ₃ -C ₆ H ₄ | 125.48 | 8.748 | –8.748 | –0.887 | 7.86 |
| 6l | p-Cl-C ₆ H ₄ | 124.74 | 8.891 | –8.891 | –1.093 | 7.79 |

^a GAP = $E_{\text{HOMO}} - E_{\text{LUMO}}$

nearly similar HOMO energies but shows variation in LUMO energies (i.e., electron affinity ‘EA’ of organic molecule) corresponds to substituents present on ring **D**. The donor chromophore increases the electron density of rest molecule hence, ultimately electron affinity i.e. LUMO energy decreases. Similarly acceptor chromophore decreases the electron density of rest molecule hence, electron affinity i.e. LUMO energy increases. For instance compound **6a** having donor chromophore (–OCH₃) on ring **D** shows lower LUMO energy (0.855 eV) and playing important role in increasing electron density hence increases stability and reactivity of this molecule. Compound **6g** having acceptor chromophore (–NO₂) shows higher LUMO energy (1.802 eV), lower electron density hence decreases stability and reactivity of this molecule.

The 3D picture (molecular modeling) of representative compound **6a** is shown in Fig. 1. The heat of formation values indicates that comp. **6a**, **6c** and **6i** are thermodynamically more stable as compared to other compounds (**6b**, **6d**,

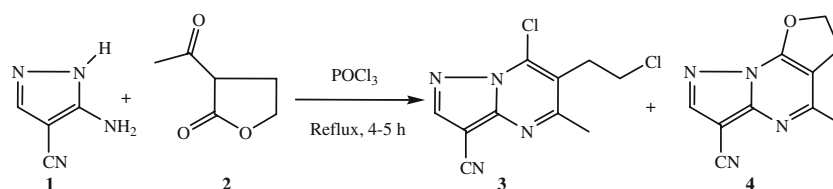
**Fig. 1** 3D-picture of compound **6a**

6e, **6f**, **6g**, **6h**, **6j**, **6k** and **6l**) (Table 1). From Table 1, It is clearly observed that; the ionization potential of **6** are in between 8–9 eV, hence may be used as potential candidates in the semiconductor [21]. Encouraging from this results, we undertook the synthesis of pyrazolo-pyrrolo-pyrimidine (PPP) derivatives **6**, starting with precursor **3**.

Chemistry

Condensation of α -acetyl- γ -butyrolactone **2** with 2-aminoheterocycles have been described in literature [17, 22], however this condensation of it with 5-amino-1*H*-pyrazole-4-carbonitrile **1** have been little explored. One pot cyclocondensation of α -acetyl- γ -butyrolactone **2** with 5-amino-1*H*-pyrazole-4-carbonitrile **1** furnished a mixture of two compounds **3** and **4** which are separated by column chromatography eluting with hexane/ethyl acetate (9:1). Cyclocondensation of this lactone with 2-aminoheterocycle under similar reaction condition did not yielded compound **4** [17] (Scheme 1).

Structures of **3** and **4** were assigned by spectroscopic characterization. For instance ¹H NMR of compound **3** shows singlet at 8.83 δ corresponds to aromatic proton of pyrazole ring, two triplets at 3.90 δ and 3.32 δ corresponds to protons of aliphatic side chain and singlet at 2.76 δ corresponds to three protons of methyl group. The mass spectrum of **3** shows a molecular ion peaks m/z at 255 [M^+] and also peaks at 257 [$M+2$] and 259 [$M+4$] due to presence of two chlorine atom. The sharp band at 2,227 cm^{-1} in IR spectrum of **3** clearly indicate the presence of –CN group. The ¹H NMR Compound **4** shows singlet at 8.72 δ due to aromatic proton in pyrazole ring and two triplets at 3.79 and 3.50 δ due to four proton of newly annulated furan

Scheme 1 Synthesis of pyrazolopyrimidines

ring and the singlet at 2.76 δ corresponds to three proton of methyl group. The $-\text{CN}$ group is observed at 2224 cm^{-1} in its IR spectrum. The formation of compound **4** can be rationalized by following mechanism (Fig. 2). The mechanism proceeds through the formation of Schiff base **A** which is isomerized by proton transfer to a more stable transient intermediate **B**. The secondary nitrogen of the pyrazole ring then attack on the lactone carbonyl resulted in the opening of lactone to form a phosphate ester on the pyrimidine ring **C**, which is subsequently displaced during the intramolecular cyclization to furnish compound **4**.

After establishing structure of **3** and **4**, the dichloro compound **3** having two replaceable chlorine groups is fused with various aniline and /or substituted anilines at $110\text{--}120^\circ\text{C}$, for 15–20 min. to afford title compounds 8-aryl-5-methyl-7,8-dihydro-6*H*-pyrazolo[1,5-*a*]pyrrolo[3,2-*e*]pyrimidine-3-carbonitriles **6a–l** in 73–86% yields (Scheme 2).

It is interesting to observe that the $-\text{NH}_2$ acted as bidentate nucleophile to give $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}\text{Ar}$ reaction and both chlorines in **3** were displaced. Compounds **6** are characterized by spectroscopic and analytical methods. In this reaction we have chosen anilines with electron-accepter and electron-donor groups to study their effect on absorption and emission in obtained compounds **6a–l**.

Photophysical Properties

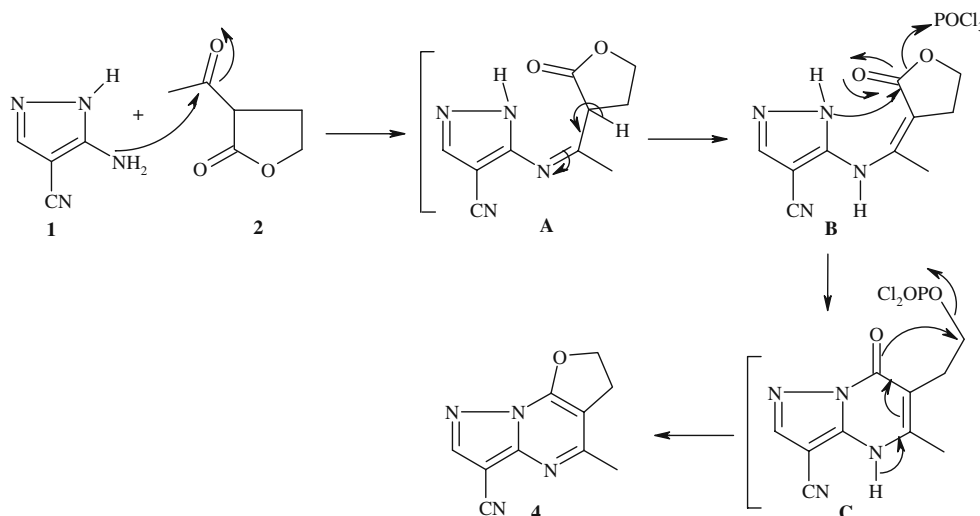
The UV absorption and emission of compounds **6a–l** are studied in polar aprotic solvent (DMF). Fluorescence

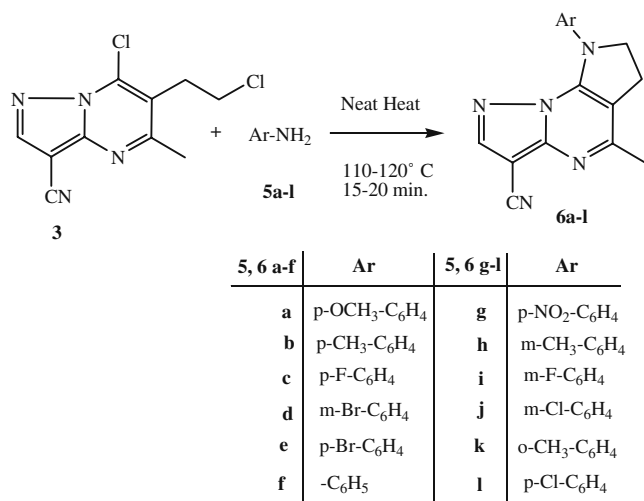
quantum yield of each are determined by standard literature procedure using quinine sulphate as reference standard [23, 24] (Table 2).

The charge is more concentrated on ring **D** as compare to ring **A**, **B** and **C** (Fig. 1). The donor/ acceptor chromophores on ring **D** is playing important role in increasing/decreasing the electron density. The ring **A** is having strong electron withdrawing $-\text{CN}$, which make facile charge delocalization in the molecules, increases the stability and reactivity of the molecule and shows high quantum yields in **6**. It is noted that compound **6a** having strong donor chromophore $-\text{OCH}_3$ at C_4 -position of ring **D** facilitates the charge delocalization via $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition hence, fluoresces at higher wavelength (457 nm) and shows highest quantum yield ($\Phi_{\text{F}}=0.30$), while compound **6g** having strong acceptor chromophore $-\text{NO}_2$ at C_4 -position of ring **D** restricts the charge delocalization hence, fluoresces at lower wavelength (383 nm) and shows lowest quantum yield ($\Phi_{\text{F}}=0.15$). All other compounds shows fluorescence and quantum yield with respect to their chromophores ($\Phi_{\text{F}}=0.15\text{--}0.29$). The comparative absorption and emission spectra of **6a** and **6g** is depicted in Fig. 3.

Thermal Properties

The organic compounds which are to be used in OLEDs and opto-electronic applications should be thermally and chemically stable. Thermal analysis of compounds **6a–l**, by differential scanning calorimetry (DSC) revealed that they

Fig. 2 Mechanism of compound **4**



Scheme 2 Synthesis of pyrazolo-pyrrolo-pyrimidines (PPP)

are thermally stable compounds up to 350 °C and also possesses high melting points and high crystallization temperature.

Conclusion

In conclusion, we have successfully synthesized PPP derivatives having excellent photophysical properties and are depends upon nature of substituents present on ring **D**. For instance, the strong donor chromophores on ring **D** of compound **6** shows lower LUMO energy, shifts absorption and emission maximum to red (Bathochromic shift), hence shows high quantum yields. Similarly strong acceptor

Table 2 The photophysical data for electronic absorption (UV λ_{Max}), fluorescence (Em. λ_{Max}) and quantum yield (Φ_{F}) of compounds **3**, **4** and **6a-l** for 0.1 M Conc. in DMF as a solvent at 25 °C

| Comp. | Ar | UV λ_{Max} /nm | Em. λ_{Max} /nm | Φ_{F} |
|-----------|---|-------------------------------|--------------------------------|-------------------|
| 3 | – | 322 | 392 | 0.11 |
| 4 | – | 318 | 387 | 0.10 |
| 6a | p-OCH ₃ -C ₆ H ₄ | 371 | 457 | 0.30 |
| 6b | p-CH ₃ -C ₆ H ₄ | 364 | 435 | 0.29 |
| 6c | p-F-C ₆ H ₄ | 363 | 433 | 0.27 |
| 6d | m-Br-C ₆ H ₄ | 370 | 399 | 0.18 |
| 6e | P-Br-C ₆ H ₄ | 371 | 425 | 0.25 |
| 6f | -C ₆ H ₅ | 373 | 424 | 0.24 |
| 6g | p-NO ₂ -C ₆ H ₄ | 319 | 383 | 0.15 |
| 6h | m-CH ₃ -C ₆ H ₄ | 377 | 424 | 0.24 |
| 6i | m-F-C ₆ H ₄ | 374 | 408 | 0.21 |
| 6j | m-Cl-C ₆ H ₄ | 369 | 403 | 0.20 |
| 6k | o-CH ₃ -C ₆ H ₄ | 330 | 397 | 0.17 |
| 6l | p-Cl-C ₆ H ₄ | 372 | 427 | 0.26 |

chromophores on ring **D** of compound **6** shows higher LUMO energy, shifts absorption and emission maximum to blue (Hypsochromic shift) and low quantum yields. Another interesting feature is that halo-substituted derivative has less fluorescence quantum yields than that of methoxy substituted compound. This could be due to quenching of fluorescence with halogen atom as the substitution. The efficient photophysical property makes pyrazolo-pyrrolo-pyrimidine (PPP) derivatives a promising family of materials which may be useful in OLEDs [25] and opto-electronic applications [26, 27].

Experimental

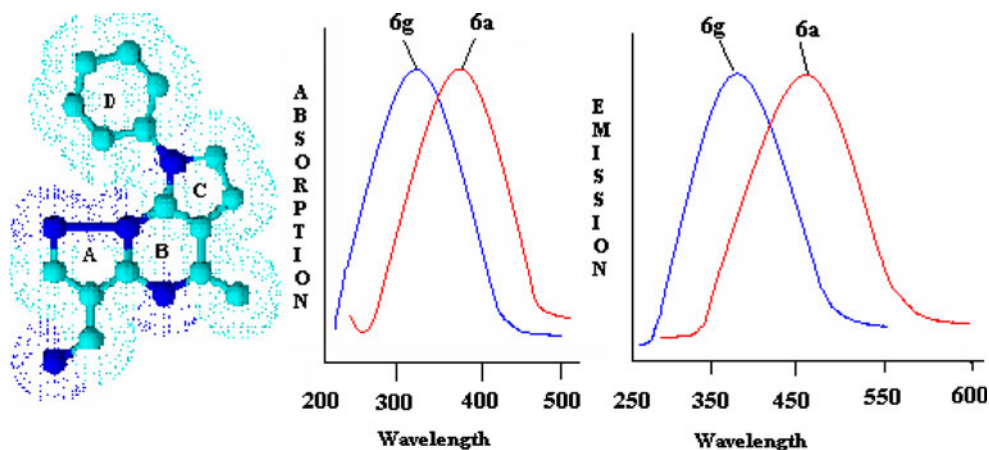
General

Melting points were determined on a Gallenkamp Melting Point Apparatus in open capillary tubes and are uncorrected. The ¹H and ¹³C NMR spectra were recorded on a Varian XL-300 spectrometer (300 MHz, 75 MHz respectively). Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given in δ -units. The solvent for NMR spectra was deuteriochloroform (CDCl₃) or DMSO (*d*₆). Infrared spectra were taken on a Shimadzu IR-408, in potassium bromide pellets. The mass spectra were recorded on QP-2010s. UV spectra were recorded on a Shimadzu UV-1601 UV-VIS Spectrophotometer. Fluorescence spectra were recorded using RF-5301 PC Spectrofluorophotometer (150-W Xe lamp), compounds for UV and fluorescence measurements were dissolved in Dimethyl formamide (DMF). UV and fluorescence scan were recorded from 200 to 600 nm. Semiempirical molecular orbital calculations were done by semi empirical PM6 Methods, MOPAC (6, 7) program package. Determination of quantum yields: emission signals were set in relation to known area of the emission signal of quinine sulphate at pH 1. Elemental analyses were performed on a Hosli CH-Analyzer and are within ± 0.3 of the theoretical percentages. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 F₂₅₄ (Merck) plates using UV light (254 and 366 nm) for detection. Column chromatography was carried out on silica gel (s.d. Fine Chemicals, 60–120 mesh powder). Starting materials were obtained from commercial suppliers and used without further purification. Common grade chemicals and starting materials are either commercially available and were used without further purification or prepared by standard literature procedures.

General Procedure for the Synthesis of Compound (3) and (4)

A mixture of 5 amino-1H-pyrazole-4-carbonitrile **1** (0.01 mol, 1.07 g) and α -acetyl - γ -butyrolactone **2**

Fig. 3 The comparative absorption (UV λ_{Max}) and emission (Em λ_{Max}) spectra of compounds (6a) and (6g) respectively



(0.01 mol, 1.07 mL) in POCl_3 (5 mL) was heated under reflux for 4–5 h. After completion of reaction (TLC Check), the reaction mass was allowed to cool, excess POCl_3 was evaporated under reduced pressure, obtained mass was quenched in ice-cold water (10 ml) to give solid precipitate. It contains two compounds according to TLC analysis (Rf value: 0.92 and 0.69 in hexane/ethyl acetate = 9:1). This mixture was separated by column chromatography (Silica-gel: 60–120 mesh, eluent: hexane/ethyl acetate = 9:1).

Chloro-6-(2-chloroethyl)-5-methylpyrazolo [1,5-a] pyrimidine-3-carbonitrile (3)

Yield: 1.91 g (75%); Colorless prism; mp 268–269 °C; IR (KBr): 3427 w, 3107 m, 2227 m, 1614 m, 1541 w, 1479 s, 1438 m, 1300 cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.76 (s, 3H, CH_3), 3.32 (t, 2H, $J=3.2$ Hz, CH_2), 3.90 (t, 2H, $J=3.2$ Hz, CH_2), 8.83 (s, 1H, Ar-H); ^{13}C NMR (DMSO- d_6) δ : 17.12, 24.18, 48.22, 96.51, 110.42, 122.17, 135.34, 137.01, 159.71, 163.62; MS (70 eV) m/z (%): 255 [M^+] (100), 257 [$\text{M}+2$] (31), 259 [$\text{M}+4$] (16). *Anal.* Calcd. for $\text{C}_{10}\text{H}_8\text{Cl}_2\text{N}_4$ (255.11): C, 47.08; H, 3.16; N, 21.96. Found: C, 47.14; H, 3.11; N, 21.95%.

5-Methyl-6,7-dihydrofuro[3,2-e]pyrazolo[1,5-a] pyrimidine-3-carbonitrile (4)

Yield: 0.20 g (10%); Colorless solid; mp 250–251 °C; IR (KBr): 3238 w, 3105 w, 2920 w, 2224 m, 1780 m, 1612 m, 1504 w, 1357 m, 1317 m, 1211 w, 927 cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.50 (s, 3H, CH_3), 3.50 (t, 2H, $J=8.1$ Hz, CH_2), 3.79 (t, 2H, $J=8.1$ Hz, CH_2), 8.72 (s, 1H, Ar-H); ^{13}C NMR (DMSO- d_6) δ : 18.05, 26.23, 76.45, 97.47, 108.53, 125.10, 137.17, 138.21, 158.45, 168.07; MS (70 eV) m/z (%): 200 [M^+] (100). *Anal.* Calcd. for $\text{C}_{10}\text{H}_8\text{N}_4\text{O}$ (200.20): C, 60.00; H, 4.03; N, 27.99. Found: C, 60.06; H, 3.99; N, 28.03%.

General Procedure for the Synthesis of Compounds (6a–I)

A mixture of compound 3 (0.01 mol, 2.55 g) and corresponding anilines 5a–I (0.01 mol) was fused at 110–120 °C for 15–20 min. After completion of reaction (TLC Check), the reaction mass was allowed to cool, obtained crude solid was stirred in cold methanol (10 mL) for 5–10 min. Filtered the separated solid, dried under high vacuum and recrystallized from suitable solvent ethanol: DMF to furnish compounds 6a–I in 73–86% yields.

8-(4-Methoxyphenyl)-5-methyl-7,8-dihydro-6H-pyrazolo [1,5-a]pyrrolo[3,2-e] pyrimidine-3-carbonitrile (6a)

Yield: 2.34 g (77%); recrystallized from ethanol/DMF (9:1) to afford colorless needle; mp 278–279 °C; IR (KBr): 3117 w, 3037 w, 2965 w, 2920 m, 2226 m, 1839 m, 1614 m, 1588 m, 1512 m, 1272 w, 1207 w, 1158 m, 919 cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.33 (s, 3H, CH_3), 2.81 (s, 3H, OCH_3), 3.27 (t, 2H, $J=9$ Hz, CH_2), 4.29 (t, 2H, $J=9$ Hz, CH_2), 7.20 (m, 4H, Ar-H), 8.37 (s, 1H, Ar-H); ^{13}C NMR (DMSO- d_6) δ : 18.12, 25.45, 48.78, 59.71, 99.23, 108.25, 118.07 (2 C's), 121.63 (2 C's), 127.10, 134.42, 137.58, 144.08, 148.23, 160.41, 169.11; MS (70 eV) m/z (%): 305 [M^+] (100). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_5\text{O}$ (305.34): C, 66.87; H, 4.95; N, 22.94. Found: C, 66.85; H, 4.96; N, 22.92%.

5-Methyl-8-p-tolyl-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo [3,2-e]pyrimidine-3-carbonitrile (6b)

Yield: 2.25 g (78%); recrystallized from ethanol/DMF (8:2) to afford white solid; mp 262–263 °C; IR (KBr): 3111 w, 3034 w, 2960 m, 2918 w, 2220 m, 1830 m, 1583 m, 1512 m, 1276 w, 1203 m, 1166 m, 918 m, 817 w, 628 cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.34 (s, 3H, CH_3), 3.42 (s, 3H, CH_3), 3.24 (t, 2H, $J=8.1$ Hz, CH_2), 4.31 (t, 2H, $J=8.1$ Hz, CH_2), 7.23 (m, 4H, Ar-H), 8.42 (s, 1H, Ar-H);

^{13}C NMR (DMSO- d_6) δ : 19.08, 24.26, 26.22, 49.45, 98.42, 109.62, 119.17 (2 C's), 124.08, 126.63, 128.82 (2 C's), 134.25, 137.91, 142.35, 160.12, 169.36; MS (70 eV) m/z (%): 289 [M^+] (100). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_5$ (289.34): C, 70.57; H, 5.23; N, 24.20. Found: C, 70.61; H, 5.22; N, 24.22%.

8-(4-Fluorophenyl)-5-methyl-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo[3,2-e] pyrimidine-3-carbonitrile (**6c**)

Yield: 2.19 g (75%); recrystallized from ethanol/DMF (9:1) to yield colorless solid; mp 274–275 °C; IR (KBr): 3107 w, 2945 m, 2899 m, 2214 m, 1627 m cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.49 (s, 3H, CH_3), 3.30 (t, 2H, $J=8.1$ Hz, CH_2), 4.41 (t, 2H, $J=8.1$ Hz, CH_2), 7.37 (d, 2H, $J=8.4$ Hz, Ar-H), 7.72 (d, 2H, $J=8.4$ Hz, Ar-H), 8.53 (s, 1H, Ar-H); MS (70 eV) m/z (%): 293 [M^+] (98). *Anal.* Calcd. for $\text{C}_{16}\text{H}_{12}\text{FN}_5$ (293.31): C, 65.52; H, 4.12; N, 23.88. Found: C, 65.50; H, 4.11; N, 23.91%.

8-(3-Bromophenyl)-5-methyl-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo[3,2-e] pyrimidine-3-carbonitrile (**6d**)

Yield: 2.58 g (73%); recrystallized from ethanol/DMF (7:3) to afford white solid; mp 269–270 °C; IR (KBr): 2958 w, 2939 w, 2895 w, 2215 m, 1617 m, 1611 m, 1512 m, 1358 m cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.41 (s, 3H, CH_3), 3.22 (t, 2H, $J=8$ Hz, CH_2), 4.30 (t, 2H, $J=8$ Hz, CH_2), 7.31 (m, 3H, Ar-H), 7.50 (s, 1H, Ar-H), 8.34 (s, 1H, Ar-H); MS (70 eV) m/z (%): 354 [M^+] (100), 356 [$\text{M}+2$] (36). *Anal.* Calcd. for $\text{C}_{16}\text{H}_{12}\text{BrN}_5$ (354.21): C, 54.26; H, 3.41; N, 19.77. Found: C, 54.21; H, 3.39; N, 19.81%.

8-(4-Bromophenyl)-5-methyl-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo[3,2-e] pyrimidine-3-carbonitrile (**6e**)

Yield: 2.79 g (79%); recrystallized from ethanol/DMF (9:1) to afford colorless solid; mp 258–259 °C; IR (KBr): 3088 m, 2933 w, 2218 m, 1622 m, 1570 m, 1518 m, 1487 w cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.43 (s, 3H, CH_3), 3.28 (t, 2H, $J=9$ Hz, CH_2), 4.33 (t, 2H, $J=9$ Hz, CH_2), 7.28 (d, 2H, $J=8.4$ Hz, Ar-H), 7.57 (d, 2H, $J=8.4$ Hz, Ar-H), 8.42 (s, 1H, Ar-H); MS (70 eV) m/z (%): 354 [M^+] (75), 256 [$\text{M}+2$] (93). *Anal.* Calcd. for $\text{C}_{16}\text{H}_{12}\text{BrN}_5$ (354.31): C, 54.26; H, 3.41; N, 19.77. Found: C, 54.25; H, 3.47; N, 19.75%.

5-Methyl-8-phenyl-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo[3,2-e]pyrimidine-3-carbonitrile (**6f**)

Yield: 2.25 g (82%); recrystallized from ethanol/DMF (8:2) to afford colorless solid; mp 283–284 °C; IR (KBr): 3398 w, 3063 w, 2964 m, 2864 m, 2212 m, 1629 s,

1610 m, 1514 s, 1280 m cm^{-1} . ^1H NMR (DMSO- d_6) δ : 2.42 (s, 3H, CH_3), 3.28 (t, 2H, $J=8.7$ Hz, CH_2), 4.33 (t, 2H, $J=8.7$ Hz, CH_2), 7.29–7.38 (m, 5H, Ar-H), 8.38 (s, 1H, Ar-H); MS (70 eV) m/z (%): 275 [M^+] (100). *Anal.* Calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_5$ (275.32): C, 69.80; H, 4.76; N, 25.44. Found: C, 69.87; H, 4.71; N, 25.45%.

5-Methyl-8-(4-nitrophenyl)-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo[3,2-e] pyrimidine-3-carbonitrile (**6g**)

Yield: 2.49 g (78%); recrystallized from ethanol/DMF (9:1) to yield white solid; mp 288–289 °C; IR (KBr): 3118 w, 2971 w, 2927 m, 2217 m, 1612 m, 1516 m, 1369 m, 1319 m cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.48 (s, 3H, CH_3), 3.29 (t, 2H, $J=8.1$ Hz, CH_2), 4.44 (t, 2H, $J=8.1$ Hz, CH_2), 7.62 (d, 2H, $J=8.4$ Hz, Ar-H), 7.87 (d, 2H, $J=8.4$ Hz, Ar-H), 8.72 (s, 1H, Ar-H). MS (70 eV) m/z (%): 320 [M^+] (100). *Anal.* Calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_6\text{O}_2$ (320.31): C, 60.00; H, 3.78; N, 26.24. Found: C, 60.07; H, 3.77; N, 26.21%.

5-Methyl-8-*m*-tolyl-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo[3,2-e]pyrimidine-3-carbonitrile (**6h**)

Yield: 2.25 g (78%); recrystallized from ethanol/DMF (8:2) to afford colorless prism; mp 271–272 °C; IR (KBr): 3047 w, 2953 w, 2918 m, 2216 m, 1616 m, 1585 m, 1514 w, 1315 m cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.37 (s, 3H, CH_3), 2.82 (s, 3H, CH_3), 3.50 (t, 2H, $J=8.1$ Hz, CH_2), 3.81 (t, 2H, $J=8.1$ Hz, CH_2), 7.38 (m, 3H, Ar-H), 7.49 (s, 1H, Ar-H), 8.42 (s, 1H, Ar-H). MS (70 eV) m/z (%): 289 [M^+] (100). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_5$ (289.34): C, 70.57; H, 5.23; N, 24.20. Found: C, 70.60; H, 5.21; N, 24.23%.

8-(3-Fluorophenyl)-5-methyl-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo[3,2-e] pyrimidine-3-carbonitrile (**6i**)

Yield: 2.46 g (84%); recrystallized from ethanol/DMF (9:1) to afford colorless prism; mp 257–258 °C; IR (KBr): 2967 w, 2947 m, 2893 w, 2213 m, 1621 m, 1600 s, 1506 m, 1362 m cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.46 (s, 3H, CH_3), 3.29 (t, 2H, $J=8.4$ Hz, CH_2), 4.35 (t, 2H, $J=8.4$ Hz, CH_2), 7.34 (m, 3H, Ar-H), 7.57 (s, 1H, Ar-H), 8.40 (s, 1H, Ar-H). MS (70 eV) m/z (%): 293 [M^+] (100). *Anal.* Calcd. for $\text{C}_{16}\text{H}_{12}\text{FN}_5$ (293.31): C, 65.52; H, 4.12; N, 23.88. Found: C, 65.57; H, 4.09; N, 23.90%.

8-(3-Chlorophenyl)-5-methyl-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo[3,2-e] pyrimidine-3-carbonitrile (**6j**)

Yield: 2.65 g (86%); recrystallized from ethanol/DMF (8:2) to afford colorless needle; mp 276–277 °C; IR (KBr): 2963 w, 2949 w, 2890 w, 2211 m, 1625 m, 1607 m, 1516 s, 1370 m cm^{-1} ; ^1H NMR (DMSO- d_6) δ : 2.44 (s, 3H, CH_3),

3.27 (t, 2H, J=9 Hz, CH₂), 4.34 (t, 2H, J=9 Hz, CH₂), 7.32 (m, 3H, Ar-H), 7.55 (s, 1H, Ar-H), 8.39 (s, 1H, Ar-H); MS (70 eV) *m/z* (%): 309 [M⁺] (100), 311 [M+2] (35). *Anal.* Calcd. for C₁₆H₁₂ClN₅ (309.76): C, 62.04; H, 3.90; N, 22.61. Found: C, 62.07; H, 3.89; N, 22.61%.

5-Methyl-8-o-tolyl-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo[3,2-e]pyrimidine-3-carbonitrile (6k)

Yield: 2.31 g (80%); recrystallized from ethanol/DMF (9:1) to afford white needle; mp 283–284 °C; IR (KBr): 3053 w, 2955 w, 2860 w, 2216 m, 1600 m, 1512 s, 1318 m cm⁻¹; ¹H NMR (DMSO-d₆) δ: 2.49 (s, 3H, CH₃), 2.51 (s, 3H, CH₃), 3.39 (t, 2H, J=9 Hz, CH₂), 4.42 (t, 2H, J=9 Hz, CH₂), 7.41 (m, 4H, Ar-H), 8.39 (s, 1H, Ar-H). MS (70 eV) *m/z* (%): 289 [M⁺] (100). *Anal.* Calcd. for C₁₇H₁₅N₅ (289.34): C, 70.57; H, 5.23; N, 24.20. Found: C, 70.61; H, 5.19; N, 24.20%.

8-(4-Chlorophenyl)-5-methyl-7,8-dihydro-6H-pyrazolo[1,5-a]pyrrolo[3,2-e]pyrimidine-3-carbonitrile (6l)

Yield: 2.25 g (73%); recrystallized from ethanol/DMF (8:2) to afford colorless solid; mp 275–276 °C; IR (KBr): 3092 w, 2937 w, 2221 m, 1627 m, 1576 m, 1523 w, 1491 m cm⁻¹; ¹H NMR (DMSO-d₆) δ: 2.45 (s, 3H, CH₃), 3.29 (t, 2H, J=9 Hz, CH₂), 4.37 (t, 2H, J=9 Hz, CH₂), 7.30 (d, 2H, J=8.1 Hz, Ar-H), 7.59 (d, 2H, J=8.1 Hz, Ar-H), 8.50 (s, 1H, Ar-H). MS (70 eV) *m/z* (%): 309 [M⁺] (100), 311 [M+2] (33). *Anal.* Calcd. for C₁₆H₁₂ClN₅ (309.76): C, 62.04; H, 3.90; N, 22.61. Found: C, 62.09; H, 3.87; N, 22.66%.

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