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The synthesis of new pyrrolo[1,2-*a*]perimidin-10-one dyes *via* two convenient routes and its characterizations

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ABSTRACT

Efficient synthesis of pyrrolo[1,2-*a*]perimidin-10-ones (**4, 8**) are accomplished *via* two new convenient methods in moderate yields. The first method is the reaction of oxalyl chloride with heterocyclic ketene aminals (HKAs) containing perimidine moiety (**3**), and the second is the reaction of 1,8-naphthalenediamine (**1**) with 2-alkoxycarbonylmethylene substituted furan-3-ones (**7**). The visible absorption spectrums of **4** and **8** were dominated by the characteristic perimidines bands in the region 381–439 nm. While compounds **4b-d** show thermal stability up to 250 °C, compounds **8** are stable up to 216–235 °C. The structures of all products were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopic methods, in case of **8b** also by XRD analysis.

1. Introduction

The importance of substituted pyrroles in organic chemistry is well-known. Pyrrol-2-ylidenes are especially interesting structures, and this unit is found in many vital natural compounds (vitamin B_{12}, prodigiosins), natural colorants (porphyrins, chlorophylls) and synthetic colorants (BODIPY dyes).

Pyrrolo[1,2-*a*]perimidin-10-one framework is an integral part of the structure of some patented dyes and pigments recommended for a wide range of industrial plastics [1–5]. They exhibit shades of colour from red to orange. Pyrroloperimidine-containing polymers have contributed to the remarkable growth of interest in coloring materials, luminescent sensors, organic light emitting diodes and other optoelectronic devices [4,6,7]. Consequently, pyrrolo[1,2-*a*] perimidines are interesting compounds from the viewpoint of both their reactions and applications.

Several methods have been reported for construction of the pyrrolo[1,2-*a*]perimidine skeleton. All the methods are based on naphthalene-1,8-diamine (**1**) chemistry [2,4,7–15]. These proceed in moderate yields by refluxing at high temperatures, mostly in the presence of various catalysts.

In this work, we aimed to prepare new pyrrolo[1,2-*a*]perimidin-10-ones and their spectroscopic characterization *via* two convenient methods. The first method is the reaction of oxalyl chloride with heterocyclic ketene aminals (HKAs) containing perimidine moiety, and the second is the reaction of **1** with 2-alkoxycarbonylmethylene substituted furan-3-ones.

2. Experimental

Solvents and all other chemical reagents were purchased from Merck, Sigma, Aldrich and Fluka. Solvents were dried by refluxing with the appropriate drying agents and distilled before use. The reactions were followed by TLC (Silica gel, aluminium sheets 60 F_{254}, Merck). Melting points were uncorrected and recorded on Electrothermal 9200 digital melting point apparatus. Microanalyses were performed on a Leco-932 CHNS-O Elemental Analyser. A Jasco 460 or Shimadzu 8400 FT-IR Spectrophotometer were used for IR spectra (4000-400 cm^{-1}). The ^{1}H and ^{13}C NMR spectra were measured with Bruker Avance III 400 MHz spectrometers and the chemical shifts were recorded in ppm units. Thermal data were obtained by using a Setaram Labsys TG-DSC/DTA thermobalance in N_2 atmosphere. Single crystal diffraction measurements were performed on Bruker AXS APEX diffractometer [16]. Diffraction data were collected over the full sphere and were corrected for absorption. The crystal structure was solved by direct methods and refined by using SHELXS-97 and SHELXL-97 crystallographic

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software packages [17,18]. 2,3-Furandiones (**5**) were synthesized according to published methods for the synthesis of **7a,b** [19,20].

2.1. General procedure for the synthesis of compound **4**

Solutions of 3**a-d** (1 mmol) and oxalyl chloride (0.127 g, 1 mmol) in CH_3CN (60 ml) were stirred for 1 h at 50 °C. after removal of the solvent, the residue was crystallized from corresponding solvent to give pure **4**.

2.1.1. 8-Acetyl-9-hydroxy-10H-pyrrolo[1,2-a]perimidin-10-one (**4a**)

Data for **4a**: Recrystallized from DMF, orange crystals, yield 0.248 g, 89%; m.p: 312 °C. FT-IR (KBr): ν_{max}: 3306 (OH), 1765 (C=O, lactam), 1703 (C=O, acetyl), 1645, 1622 cm^{-1} (C=N and C=C); ^1H NMR (DMSO-d_6): 12.23 (s (br), 1H, OH was D_2O exchangeable), 8.34–7.50 (m, 6H, Ar–H), 2.42 ppm ($COCH_3$); ^{13}C NMR (DMSO-d_6): 192.08 (C=O, acetyl), 173.30 (C=C–OH), 160.03 (C=O, lactam), 152.08, 137.19, 133.59, 128.42, 128.18, 124.37, 123.99, 117.21, 115.82, 113.66, 110.19, (C=C), 28.65 ppm (CH_3). Anal. Calcd. For $C_{16}H_{10}N_2O_3$: C, 69.06; H, 3.62; N, 10.07 Found: C, 69.23; H, 3.54; N, 10.23%.

2.1.2. 8-Benzoyl-9-hydroxy-10H-pyrrolo[1,2-a]perimidin-10-one (**4b**)

Data for **4b**: Recrystallized from diethylether-hexane(1:1), red crystals, yield 0.289 g, 85%; m.p: 215 °C. FT-IR (KBr): ν_{max}: 3308 (OH), 1720 (C=O, lactam), 1673 (C=O, benzoyl), 1646, 1631 cm^{-1} (C=N and C=C); ^1H NMR (DMSO-d_6): 12.63 (s (br), 1H), 8.29–7.40 ppm (m, 11H, Ar–H); ^{13}C NMR (DMSO-d_6): 188.01 (C=O, benzoyl), 161.41 (C=C–OH), 159.78 (C=O, lactam), 148.66, 138.73, 136.29, 135.97, 135.46, 133.81, 131.05, 130.51, 129.75, 128.90, 128.56, 127.91, 124.69, 123.51, 117.46, 109.90 ppm (C=C). Anal. Calcd. For $C_{21}H_{12}N_2O_3$: C, 74.11; H, 3.55; N, 8.23 Found: C, 73.94; H, 3.75; N, 8.49%.

2.1.3. 9-Hydroxy-8-(4-methoxybenzoyl)-10H-pyrrolo[1,2-a] perimidin-10-one (**4c**)

Data for **4c**: Recrystallized from diethylether-hexane(1:1), red crystals, yield 0.318 g, 86%; m.p: 198 °C. FT-IR (KBr): ν_{max}: 3303 (OH), 1729 (C=O, lactam), 1655 (C=O, aroyl), 1638, 1628 cm^{-1} (C=N and C=C); ^1H NMR ($CDCl_3$): 13.10 (s, br, 1H), 8.55–6.94 ppm (m, 10H, Ar–H); 3.92 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$): 188.08, 185.18 (C=O), 165.17 (C=C–OH), 159.34 (C=O, lactam), 153.85, 147.50, 138.60, 136.82, 133.61, 132.56, 132.41, 131.53, 130.42, 128.57, 127.95, 125.59, 123.61, 117.46, 114.36, 110.75 (C=C), 55.68, 55.45 ppm (OCH_3). Anal. Calcd. For $C_{22}H_{14}N_2O_4$: C, 71.35; H, 3.81; N, 7.56 Found: C, 71.14; H, 3.54; N, 7.67%.

2.1.4. 8-(3,4-Dimethoxybenzoyl)-9-hydroxy-10H-pyrrolo[1,2-a] perimidin-10-one (**4d**)

Data for **4d**: Recrystallized from diethylether-hexane(1:1), red crystals, yield 0.320 g, 80%; m.p: 255 °C. FT-IR (KBr): ν_{max}: 3303 (OH), 1672, 1653, 1641 cm^{-1} (C=O, C=N); ^1H NMR (DMSO-d_6): 13.84, 12.40 (s, 1H, OH); 7.75–6.66 (m, 9H, Ar–H); 4.65 (s, 1H, CH); 3.88, 3.84 ppm (s, 6H, OCH_3); ^{13}C NMR (DMSO-d_6): 190.80, 170.89 (C=O), 163.50 (C=C–OH), 157.53 (C=O, lactam), 149.26, 134.79, 133.02, 129.23, 124.15, 122.89, 111.61, 110.70, 108.33, 105.65 (C=C), 56.38, 56.15 ppm (OCH_3). Anal. Calcd. For $C_{23}H_{16}N_2O_5$: C, 69.00; H, 4.03; N, 7.00 Found: C, 68.85; H, 3.84; N, 7.18%.

2.2. General procedure for the synthesis of compound **7**

Solutions of 2,3-dihydrofuran- 2,3-diones **5** (1 mmol) and **6** (1 mmol) in dry benzene (60 ml) were refluxed for 30 min after removal of the solvent, the residue was treated with cold methanol (20 ml, 0–5 °C) and crystallized from methanol to give pure **7**.

2.2.1. Methyl (2Z)-[4-(3,4-dimethoxybenzoyl)-5-(3,4-dimethoxyphenyl)-3-oxofuran-2(3H)-ilidene]acetate (**7c**)

Data for **7c**: Orange crystals, yield: 0.363 g, 80%; mp 172 °C. FT-IR (KBr): ν_{max}: 1722, 1697, 1668 (C=O), 1634 cm^{-1} (C=C); ^1H NMR ($CDCl_3$): 7.75–6.80 (m, 6H, Ar–H), 6.18 (s, 1H, C=CH), 3.95, 3.93, 3.91, 3.89, 3.78 (5 × s, 15H, OCH_3); ^{13}C NMR ($CDCl_3$): 188.49 (C=O, aroyl), 184.21 (C_3=O), 176.81 (C=O, ester), 163.98, 154.51, 151.32, 149.43, 149.09, 129.83, 125.73, 124.39, 118.96, 114.97, 111.48, 111.10, 110.67, 110.17, 100.16 (C=C), 56.20, 56.15, 56.07, 55.88, 55.27 (OCH_3). Anal. Calcd. For $C_{24}H_{22}O_9$: C, 63.43; H, 4.88; Found: C, 63.21; H, 4.72%.

2.2.2. Ethyl (2Z)-[4-(3,4-dimethoxybenzoyl)-5-(3,4-dimethoxyphenyl)-3-oxofuran-2(3H)-ilidene]acetate (**7d**)

Data for **7d**: Orange crystals, yield: 0.356 g, 76%; mp 150 °C. FT-IR (KBr): ν_{max}: 1718, 1695, 1670 (C=O), 1638 cm^{-1} (C=C); ^1H NMR ($CDCl_3$): 7.70–6.82 (m, 6H, Ar–H), 6.16 (s, 1H, C=CH), 4.35 (q, 2H, J = 7.1 Hz, OCH_2), 3.95, 3.92, 3.89, 3.73 (4 × s, 12H, OCH_3), 1.40 ppm (t, 3H, J = 7.1 Hz, CH_3); ^{13}C NMR ($CDCl_3$): 188.54 (C=O, aroyl), 184.26 (C_3=O), 176.79 (C=O, ester), 163.58, 154.47, 151.13, 149.41, 149.09, 129.88, 125.71, 124.36, 119.04, 115.01, 111.44, 111.08, 110.69, 110.17, 100.73 (C=C), 61.31 (OCH_2), 56.20, 56.15, 56.07, 55.90 (OCH_3), 14.24 ppm (CH3). Anal. Calcd. For $C_{25}H_{24}O_9$: C, 64.10; H, 4.88; Found: C, 64.37; H, 4.98%.

2.3. General procedure for the synthesis of compound **8**

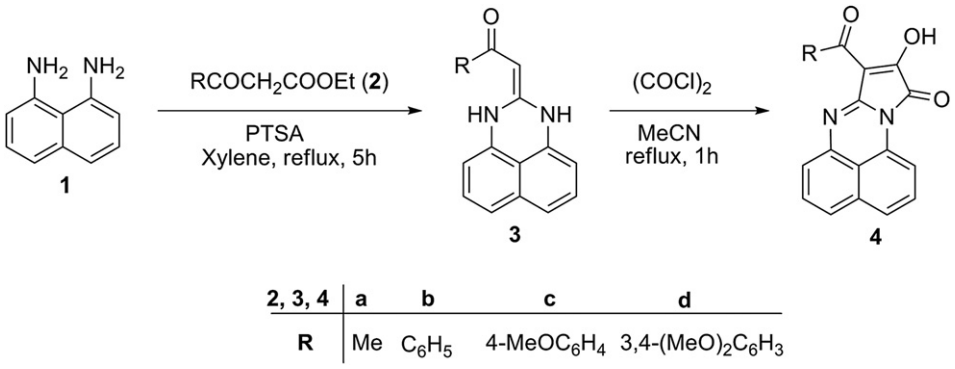
Solutions of furan-3-ones 7 (1 mmol) and naphthalene-1,8-diamine (1 mmol) in methanol (60 ml) were refluxed for 30 min the resulting solid was collected and recrystallized from *n*-butanol.

2.3.1. Methyl (2Z)-[9-hydroxy-8-(4-methoxybenzoyl)-7a-(4-methoxyphenyl)-7,7a-dihydro-10H-pyrrolo[1,2-a]perimidin-10-iliden]acetate (**8a**)

Data for **8a**: Red crystals, yield: 0.412 g, 77%; mp 185 °C. FT-IR (KBr): ν_{max}: 3441 (OH, br.), 3387 (NH), 1670, 1638 (C=O), 1631 cm^{-1} (C=N); ^1H NMR (DMSO-d_6): 14.54 (s, 1H, OH), 7.88–6.63 (m, 14H, Ar–H), 5.94 (s, 1H, C=CH), 3.82, 3.72, 3.53 (s, 9H, OCH_3); ^{13}C NMR (DMSO-d_6): 189.17 (C=O), 173.99 (C=O, ester), 159.11 (C=C–OH), 163.65, 156.21, 154.84, 139.85, 134.29, 131.80, 131.45, 131.14, 131.03, 128.55, 128.50, 126.09, 125.27, 119.70, 117.26, 117.14, 116.35, 114.00, 113.90, 109.76 (C=C), 84.85 (C=CHCOOMe), 81.63 (NH–C–N), 55.97, 55.26, 53.22 (OCH_3). Anal. Calcd. For $C_{32}H_{26}N_2O_6$: C, 71.90; H, 4.90; N, 5.24 Found: C, 71.76; H, 4.59; N, 5.02%.

2.3.2. Ethyl (2Z)-[9-hydroxy-8-(4-methoxybenzoyl)-7a-(4-methoxyphenyl)-7,7a-dihydro-10H-pyrrolo[1,2-a]perimidin-10-iliden]acetate (**8b**)

Data for **8b**: Red crystals, yield: 0.400 g, 73%; mp 196 °C. FT-IR (KBr): ν_{max}: 3435 (br, OH), 3389 (NH), 1665, 1638 (C=O), 1630 cm^{-1} (C=C); ^1H NMR (DMSO-d_6): 14.62 (s, 1H, OH), 7.78–6.63 (m, 14H, Ar–H), 5.91 (s, 1H, C=CH), 4.17 (q, 2H, J = 7.0 Hz, OCH_2), 3.87, 3.54 (s, 6H, OCH_3), 1.22 ppm (t, 3H, J = 7.0 Hz, CH_3); ^{13}C NMR (DMSO-d_6): 189.17 (C=O), 173.61 (C=O, ester), 159.11 (C=C–OH), 163.64, 156.29, 154.94, 139.85, 134.29, 131.79, 131.50, 131.18, 131.07, 128.51, 126.11, 125.25, 119.67, 117.30, 117,12, 116.35, 113.99, 113.90, 109.72, (C=C), 85.16 (C=CHCOOMe), 81.63 (NH–C–N), 62.12 (OCH_2), 55.97, 55.28 (OCH_3), 14.49 ppm (CH_3). Anal. Calcd. For $C_{33}H_{28}N_2O_6$: C, 72.25; H, 5.14; N, 5.11 Found: C, 72.38; H, 5.34; N, 5.40%.



Scheme 1. The first method of the synthesis of pyrrolo[1,2-*a*]perimidin-10-ones.

*2.3.3. Methyl (2Z)-[8-(3,4-dimethoxybenzoyl)-7a-(3,4-dimethoxyphenyl)-9-hydroxy-7,7a-dihydro-10H-pyrrolo[1,2-a] perimidin-10-iliden]acetate (**8c**)*

Data for **8c**: Red crystals, yield: 0.470 g, 79%; mp 195 °C. FT-IR (KBr): ν_{max}: 3448 (br, OH), 3385 (NH), 1670, 1655 (C=O), 1618 cm^{-1} (C=C); ^1H NMR (DMSO-d_6):14.45 (s, 1H, OH), 7.78–6.62 (m, 12H, Ar–H), 5.92 (s, 1H, C=CH), 3.83, 3.78, 3.72, 3.59, 3.53 ppm (s, 15H, OCH_3); ^{13}C NMR (DMSO-d_6): 189.25 (C=O), 173.97 (C=O, ester), 156.44 (C=C–OH), 154.56, 153.71, 148.78, 148.74, 148.61, 140.01, 134.30, 131.80, 131.24, 130.79, 128.52, 126.14, 125.26, 124.84, 119.93, 119.61, 117.36, 117.17, 116.39, 111.76, 111.40, 111.16, 111.04, 109.63 (C=C), 84.90 (C=CHCOOMe), 81.80 (NH–C–N), 56.20, 56.09, 56.02, 55.58, 53.19 ppm (OCH_3). Anal. Calcd. For $C_{34}H_{30}N_2O_8$: C, 68.68; H, 5.09; N, 4.71 Found: C, 68.39; H, 5.15; N, 4.88%.

*2.3.4. Ethyl (2Z)-[8-(3,4-dimethoxybenzoyl)-7a-(3,4-dimethoxyphenyl)-9-hydroxy-7,7a-dihydro-10H-pyrrolo[1,2-a] perimidin-10-iliden]acetate (**8d**)*

Data for **8d**: Red crystals, yield: 0.438 g, 72%; mp 183 °C. FT-IR (KBr): ν_{max}: 3443 (br, OH), 3376 (NH), 1671, 1636 (C=O), 1621 cm^{-1} (C=C); ^1H NMR (DMSO-d_6): 14.55 (s, 1H, OH), 7.78–6.63 (m, 12H, Ar–H), 5.89 (s, 1H, C=CH), 4.18 (q, 2H, J = 7.1 Hz, OCH_2), 3.83, 3.78, 3.58, 3.53 (s, 12H, OCH_3), 1.22 ppm (t, 3H, J = 7.1 Hz, CH_3); ^{13}C NMR (DMSO-d_6): 189.25 (C=O), 173.59 (C=O, ester), 156.52 (C=C–OH), 154.67, 153.68, 148.76, 148.61, 140.02, 134.30, 131.83, 130.81, 128.53, 126.16, 125.24, 124.58, 119.94, 119.57, 117.41, 116.39, 111.73, 111.38, 111.04, 109.60 (C=C), 85.20 (C=CHCOOMe), 81.79 (NH–C–N), 62.08 (OCH_2), 56.20, 56.09, 56.02, 55.58 (OCH_3), 14.50 ppm (CH_3). Anal. Calcd. For $C_{35}H_{32}N_2O_8$: C, 69.07; H, 5.30; N, 4.60 Found: C, 68.85; H, 5.05; N, 4.71%.

3. Results and discussion

3.1. Synthesis of pyrrolo[1,2-a]perimidin-10-ones

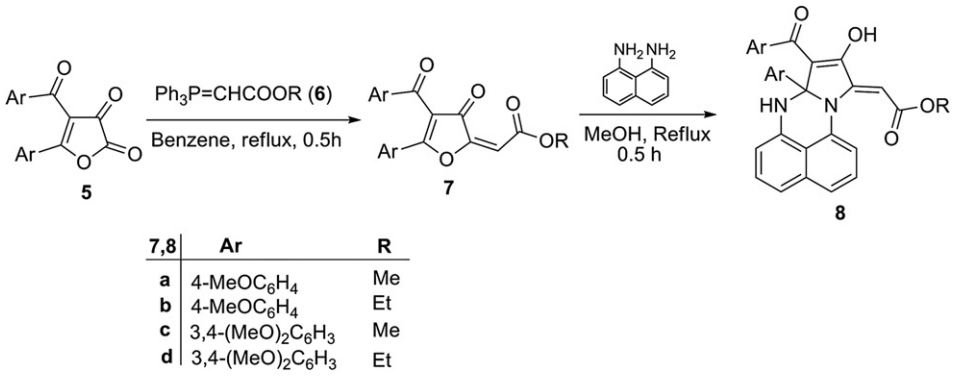
According to literatures, enaminones undergo cyclo-condensations with $OxCl_2$ to provide the corresponding pyrroles [21–23]. This method was considered as a general procedure for a new type of pyrrolo[1,2-*a*]perimidin-10-one dyes. Firstly, HKAs were prepared from **1** and corresponding β-keto esters **2** in xylene [24]. Simply heating an MeCN solution of HKAs and $OxCl_2$ led to the formation 8-acyl-9-hydroxy substituted pyrrolo[1,2-*a*]perimidin-10-ones in good yields (80–89%) as outlined in Scheme 1.

Alkyl (2*E*)-[4-aroyl-5-aryl-3-oxofuran-2(3*H*)-ylidene]acetates (**7a-d**) were prepared for the synthesis of the planned perimidine ring-system as the second-type of starting material. While **7a,b** were known compounds [25,26], **7c,d** were newly synthesized. Subsequently, compounds **7a-d** were smoothly reacted with **1** in boiling methanol to give pyrrolo[1,2-*a*]perimidin-10-ylidenes **8a-d** in good yields (72–79%), (Scheme 2). On completion of the reaction, the orange-red crude products **8** precipitated in highly pure state.

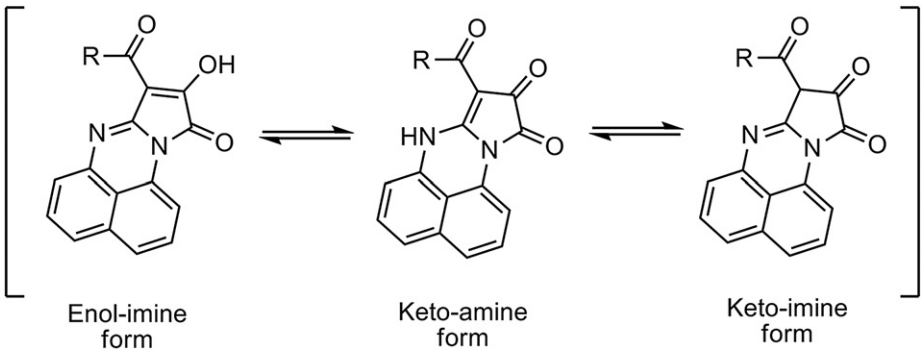
3.2. Spectral characterizations of pyrrolo[1,2-a]perimidin-10-ones

In the ^{13}C NMR spectra of **4**, lactam carbonyl carbons were clearly observed in the range of δ 157.5–160.0 ppm. Both C–signals attached to enol–OH of **4** and **8** appeared in the range of δ 156.5–159.1 ppm.

In the ^1H NMR spectra, there were no signals of **8a-d** related to tautomeric equilibrium. However, ^1H NMR signals of compound **4**



Scheme 2. The preparation of furan-3-ones (**7a-d**) and their reactions with napthalene-1,8- diamine.



Scheme 3. The possible tautomeric forms of **4** in $CDCl_3$.

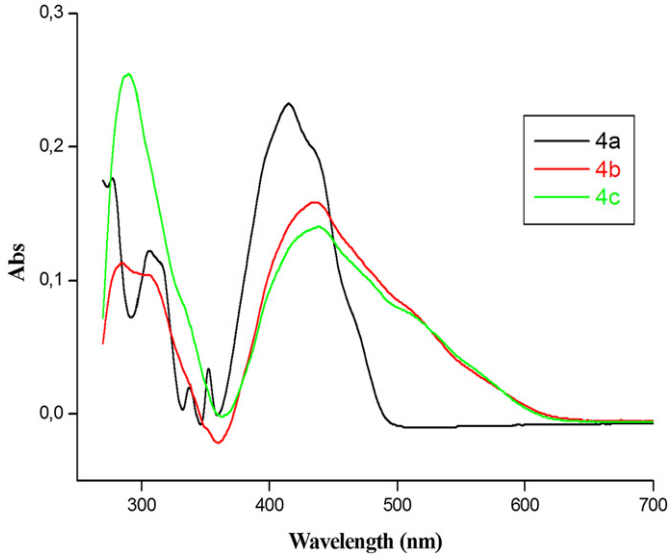


Fig. 1. UV–vis spectra of compounds **4** in DMF.

were showed evidence of all the possible tautomeric form in solution (Scheme 3).

According to the ^{1}H NMR data; compounds **4a,b** exist mainly in the keto–amine form in DMSO-d_6. NH signals of keto–amine forms of compounds **4a,b** were observed at δ 12.23 and 13.10 ppm, respectively. On the other hand, compound **4c** is in equilibrium with approximately 20% of the corresponding keto–amine form and 80% enol–imine form in $CDCl_3$. OH proton signals of enol–imine form of **4c** shows two distinct resonances at δ 8.43 and 8.45 ppm as two singlets. This observation is revealed that there are two different intramolecular hydrogen bondings between the O–H proton of enol–imine form and two different C=O groups. Moreover, in the ^{1}H NMR spectra of **4c**, there was no signal from a methine proton belonging to the keto–imine tautomer in $CDCl_3$ solution. But, **4d** showed a signal at δ 4.65 ppm from methine proton belonging to the keto–imine tautomer in DMSO-d_6 solution. In addition, NH signal of **4d** belonging to keto–amine tautomer was detected at δ 13.56 ppm.

The ^{1}H NMR spectrum of **8a** showed the O–H proton at δ 14.54, and an olefinic proton signal at δ 5.94 ppm. The three methoxy protons appeared as sharp singlets at δ 3.82, 3.72, 3.53 ppm ^{1}H NMR data of the other compounds (**8b-d**) agree with the proposed molecular structure.

The IR spectra of **4a-d** clearly showed absorption bands in the ranges of 1765–1720 cm^{-1} (C=O, lactam), 1703–1655 cm^{-1} (C=O, acyl) and 1646–1638 cm^{-1} (C=N). The O–H vibrations were observed as broad bands in the range of 3306–3303 cm^{-1}.

According to the published report, the origin of the long–wavelength absorption band of perimidines is the

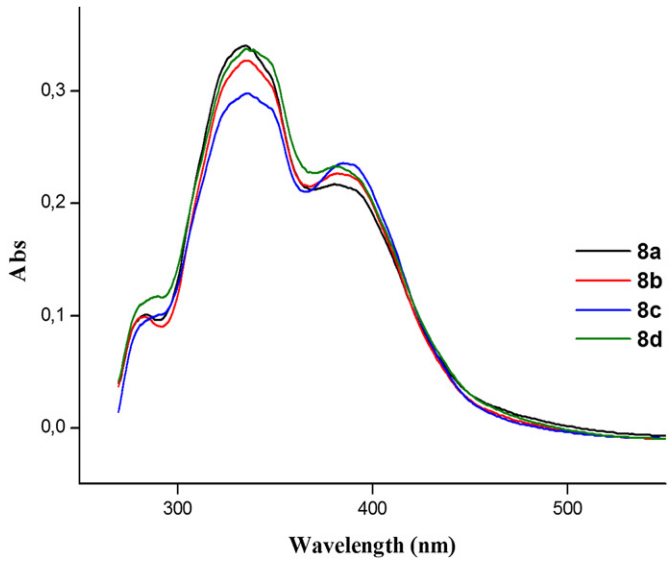


Fig. 2. UV–vis spectra of compounds **8** in DMF.

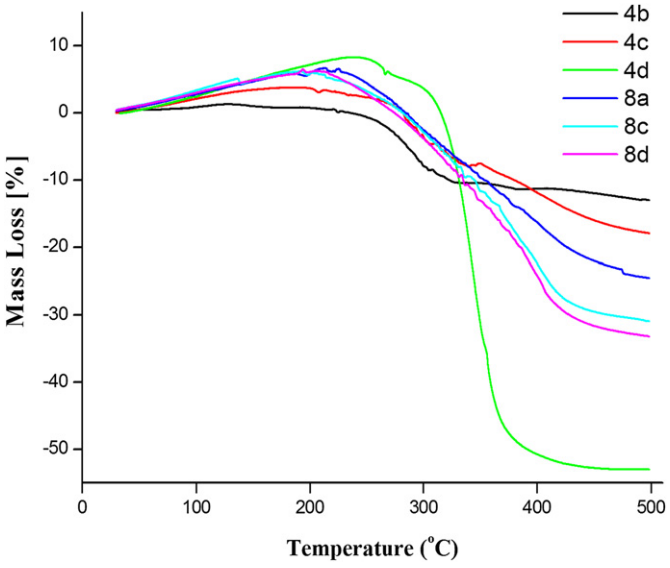


Fig. 3. Thermogravimetric analyses curve in N_2 atmosphere of pyrrolo[1,2-*a*]perimidin-10-ones.

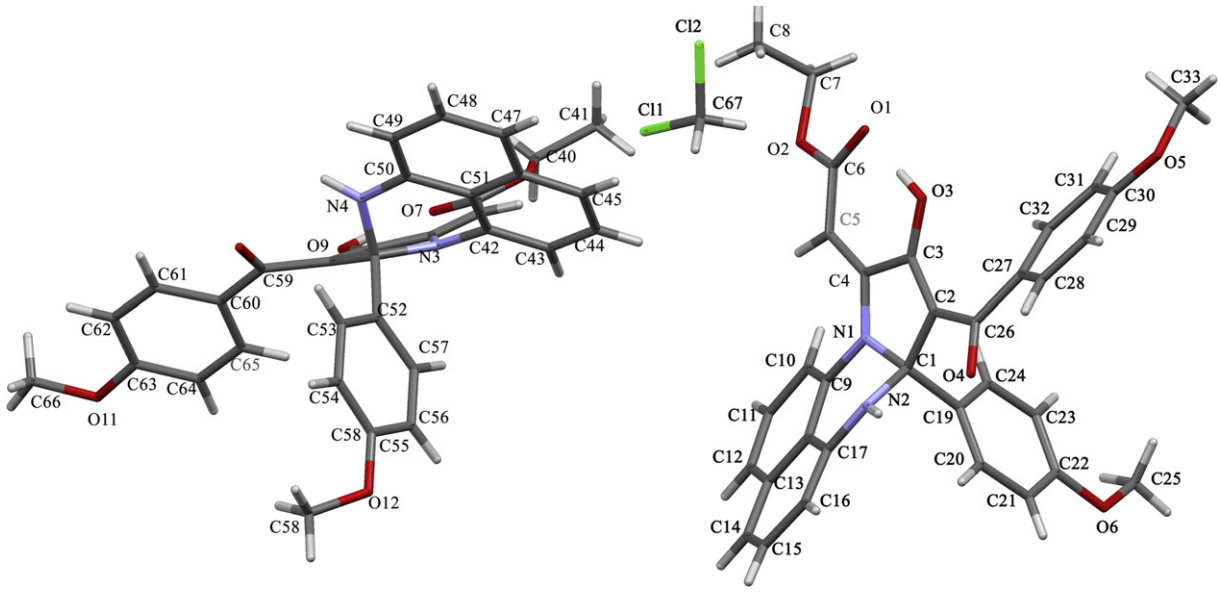


Fig. 4. Molecular structure of **8b**.

π–electron transfer from the naphthalene ring to the heteroring. This band that is responsible for the colour of the perimidines is observed about 400 nm [10].

The UV–Vis absorption spectra of **4a-c** and **8a-d** in DMF at a concentration of 1.000×10^{-5} are showed in Figs. 1 and 2, respectively. In the visible region, the molar absorption coefficients and absorption maxima of compounds **4a-c** were observed in the range 1.400×10^4 to 2.330×10^4 dm^3 mol^{-1} cm^{-1} (415–439 nm). Similarly, the visible absorption spectrums of **8a-d** were dominated by the characteristic perimidines bands in the region 381–383 nm. The molar absorption coefficients were calculated in the range of 2.170×10^4 to 2.360×10^4 dm^3 mol^{-1} cm^{-1}. There was no significant difference between them.

While compounds **4b-d** show thermal stability up to 250 °C, compounds **8** are stable up to 216–235 °C as seen in Fig. 3. The curves obtained from thermogravimetric analyses have characteristic one-step decomposition region up to 500 °C.

3.3. X-Ray crystallography

Unambiguous evidence for the structure of **8** with the atom labeling was obtained by using X-ray analysis (Fig. 4). The X-Ray crystallographic analysis show that **8b** crystallizes in triclinic system and space group *P*-1. Compound **8b** was crystallized from CH_2Cl_2-cyclohexane (1:1) for single crystal studies. So, the structure consists of the two **8b** molecules and one CH_2Cl_2 as a solvent. The inter atomic bond lengths and angles are almost similar in the two molecules. The bond distances are typical single bond character in Pyrrolidine-3-ol ring. The dihedral angle between pyrrolidine plane [Cg1: N(1)–C(1)–C(2)–C(3)–C(4)] and perimidine plane in molecule 1 is 37.2°. This value is 44.8° in molecule 2. The pyrrolidine-3-ol ring and methoxy benzene are nearly perpendicular with an angle of 81.2°. The loss of planarity of the perimidine ring is worth mentioning. The C(1) atom lies below the plane of perimidine ring in molecule of **8b** [27].

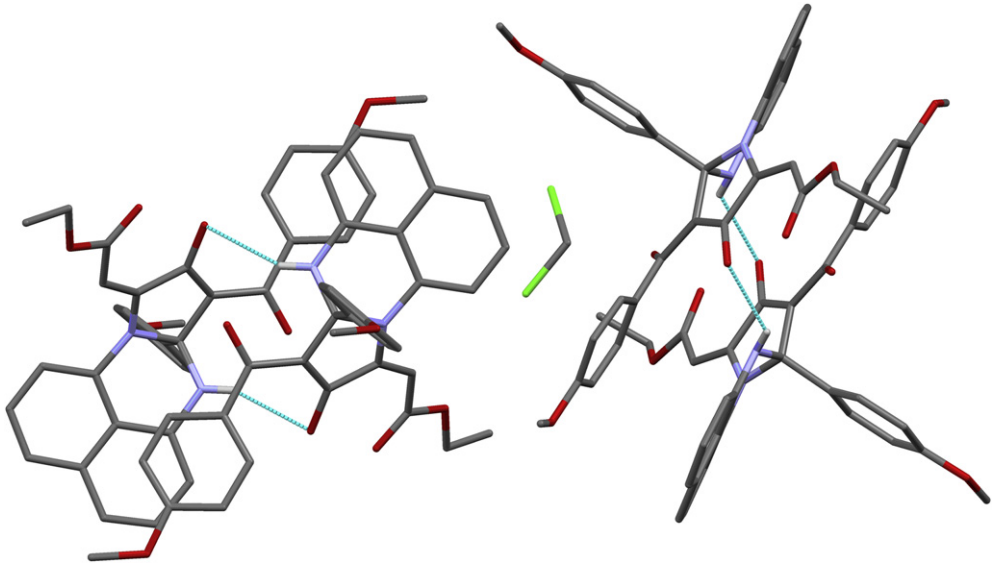


Fig. 5. Perspective view of N2–H2···O3^{i} and N4–H4···O9^{ii} interactions. Some hydrogen atoms have been omitted for clarity. (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z + 2$.

There are strong and nearly linear intramolecular hydrogen bondings O3–H3···O1 (1,64 Å, 170°) in molecule 1 and O9–H9···O7 (1,69 Å, 172°) in molecule 2. Intermolecular hydrogen bondings in two molecule (N2–H2···O3 (2.57 Å, 134°) and N4–H4···O9 (2.39 Å, 154°)) are shown in Fig. 5.

4. Conclusion

We have developed two novel and convenient routes for the synthesis of a wide range 9-hydroxy-pyrrolo[1,2-*a*]perimidin-10-ones (**4** and **8**). All compounds were characterized molecular spectroscopic methods. Compounds **4** and **8** are all vividly coloured red or orange powders. The synthetic conditions are mild allowing the preparations of novel pyrrolo[1,2-*a*]diazine derivatives.

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[27] Crystallographic data for the structural analysis of 8b has been deposited at the Cambridge Crystallographic Data Centre as deposition No. CCDC 830382. Copies of the data can be obtained, free of charge, on applicant to the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44 (1223) 336033); email: deposit@ccdc@cam.ac.uk.