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Solvent-free synthesis of aryl-substituted pyrylium salts and investigation of the auxochromes' effects on their photophysical properties

Aril-sübstitüe pirilyum tuzlarının çözücüsüz sentezi ve oksokromların fotofiziksel özellikleri üzerine etkilerinin araştırılması

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Abstract

Pyrylium compounds are structures based on an oxonium heterocycle that has been extensively studied thanks to their superior absorption and fluorescence properties. In this study, pyrylium salts were first shown to be obtained in the solvent-free medium. Six pyrylium compounds, three of which were novel, were synthesized using this method. These compounds have different auxochromes on the phenyl groups at the 2,4 and 6 positions. In the final step, the photophysical properties of these compounds were examined and the effects of basic auxochromes on pyrylium photophysics were revealed.

Keywords: Fluorescence, Pyrylium, Solvent-free synthesis, UV-Vis spectroscopy

Öz

Pirilyum bileşikleri, üstün absorpsiyon ve floresans özellikleri nedeniyle üzerinde yoğun olarak çalışılan, oksonyum hetorhalkası üzerine kurulu yapılardır. Bu çalışma kapsamında ilk olarak pirilyum tuzlarının çözücüsüz ortamda elde edilebileceği gösterildi. Bu yöntem kullanılarak üçü yeni olan altı pirilyum bileşiği sentezlendi. Bu bileşiklerin 2,4 ve 6 pozisyonlarındaki fenil gruplarında farklı oksokromlar bulunmaktadır. Son aşamada bu bileşiklerin fotofiziksel özellikleri incelendi ve temel oksokromların pirilyum fotofiziği üzerindeki etkileri ortaya konuldu.

***Anahtar kelimeler**: Floresans, Pirilyum, Çözücüsüz sentez, UV-Vis spektroskopisi*

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1. Introduction

Pyrylium core is a six-membered ring bearing a positively charged oxygen atom. Compounds based on this core have high absorption coefficients and can fluoresce strongly depending on the substituents attached to the core. Because of these superior photophysical properties, it has been used in various application areas as a photocatalyst (Hola & Ortyl, 2021), sensor (García et al., 2005; Jiménez et al., 2003; Qian et al., 2015; Yin et al., 2022), and photosensitizer (Miranda & Garcia, 1994). Unsubstituted pyrylium salt has its maximum absorption band at ca. 270 nm with a molar absorption coefficient of 9000 L·mol-1cm-1 (Burov et al., 2008; Makin et al., 1986). The attachment of aryl groups to the ring at different positions results in dramatic bathochromic shifts and increases in the molar absorption coefficient. In general, pyrylium salts tend to fluoresce strongly. However, substituents attached to the nucleus can also cause apparent changes in the fluorescence properties. The effects of different substituents and fused systems on pyrylium photophysics have been investigated by various groups (Yoshida et al., 1982; Haucke et al., 1992).

In this paper, we first introduced a solvent-free synthetic procedure to access 2,4,6-triaryl pyrylium compounds. By using this procedure, six pyrylium salts have been synthesized and their photophysical properties were investigated.

2. Material and method

2.1. Materials and instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker 400 FT-NMR spectrometer. UV/visible absorption measurements were performed on PG instruments T80 UV/visible spectrometer. Fluorescence spectra were recorded on the Shimadzu RF-5301 PC spectrofluorometer. HRMS data were collected on Agilent High-Resolution Quadrupole Time-of-Flight LC/MS.

Commercially available reagents and solvents were purchased from Sigma-Aldrich or TCI and were used without further purification or drying.

2.2. Synthesis of pyrylium salts

To a mixture of corresponding benzaldehyde (1 mmol) and acetophenone (3 mmol) was added BF_3OEt_2 (5 mmol) and heated at 120°C for one hour. The reaction mixture was allowed to cool to room temperature and its contents were transferred to a beaker using 3 ml of acetone. 30 ml of diethyl ether was added to this beaker to precipitate the mostly pure product. The solid product was filtered and washed with acetone (5 ml) and diethyl ether (15 ml). For compounds **3** and **4**, the obtained solids were further washed with 15 mL of acetone. The solids were dried at room temperature overnight.

1. Yellow solid (47%) ^{1}H NMR (400 MHz, DMSO) δ 9.19 (s, 2H), 8.62 (m, 6H), 7.89-7.82 (m, 9). ^{13}C NMR (100 MHz, DMSO) δ 169.3, 164.9,135.2, 135.0,132.0,129.8, 129.1, 128.5, 114.9

2. Red-black solid (55 %). ^{1}H NMR (400 MHz, DMSO) δ 8.51 – 8.36 (m, 8H), 7.92 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.2 Hz, 4H), 6.88 (d, J = 9.3 Hz, 2H), 3.21 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 167.5, 160.3, 156.2, 144.9, 133.8, 130.8, 127.4, 118.5, 113.3, 109.2, 40.5.

3. Red solid (23 %). ^{1}H NMR (400 MHz, DMSO) δ 10.01 (bs, 1H) 8.41 – 8.15 (m, 7H), 7.92-7.82 (m, 6H), 6.05 (d, J = 8.2 Hz, 1H), 5.93 (s, 1H), 3.21 (s, 6H). 13C NMR (100 MHz, DMSO) δ 167.6, 158.9, 156.1, 143.7, 131.5, 130.8, 128.5, 127.0, 118.3, 110.4, 106.9, 40.6.

4. Red-black solid (61 %). ^{1}H NMR (400 MHz, DMSO) δ 8.43 – 8.15 (m, 7H), 7.91-7.80 (m, 6H), 6.12 (d, J = 8.1 Hz, 1H), 5.92 (s, 1H), 3.21 (s, 6H). 13C NMR (100 MHz, DMSO) δ 167.0, 158.9, 156.9, 143.7, 132.6, 130.0, 126.0, 117.1, 108.8, 106.9, 40.6.

5. Red-black solid (58 %). ^{1}H NMR (400 MHz, DMSO) δ 8.53 – 8.42 (m, 4H), 8.24 (d, J = 8.2 Hz, 4H), 7.48 (d, J = 8.2 Hz, 4H), 6.88 (d, J = 9.3 Hz, 2H), 3.21 (s, 6H), 2.46 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 165.40, 159.21, 156.06, 144.75, 133.70, 130.58, 127.95, 127.42, 118.56, 113.25, 109.08, 40.52, 21.79. HRMS: m/z calcd. for C27H26NO [M-BF4]+: 380.2009; found: 380.2031.

6. Orange solid (43 %). ^{1}H NMR (400 MHz, DMSO) δ 8.4 (d, *J* = 8.2 Hz, 4H), 8.03-7.91 (m, 4H), 7.93-7.76 (m, 6H), 6.03 (s, 2H), 3.82-3.79 (m, 9H). ^{13}C NMR (100 MHz, DMSO) 168.0, 162.5, 135.1, 134.0, 131.9, 130.4, 130.1, 129.8, 129.6, 114.9.

2.3. Photophysical studies

A solution of the corresponding pyrylium salt in DMSO (10^{-3} M) was used as the stock solution. This solution was diluted in acetonitrile to obtain the solutions studied in photophysical studies.

The fluorescence quantum yield of the compounds was calculated by the comparative method using Rhodamine B as the fluorescence quantum yield standard ($\phi_f = 0.71$ in ethanol (Arbeloa et al., 1989)). Both Rhodamine B and the compound were excited at 400 nm for these measurements.

3. Results and discussion

3.1. Synthesis

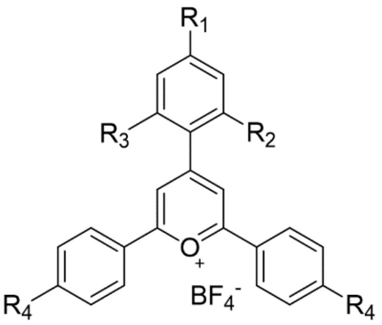
One of the most common methods to access 2,4,6-triphenyl pyrylium compounds is to heat the corresponding benzaldehyde and acetophenone in a solvent in the presence of perchloric acid or BF_3OEt_2 (Aliaga et al., 2019; Idelson et al., 2017; Lainé et al., 2006). The yields obtained by this method vary between 10-60%. When we used this procedure to synthesize 2,4,6-triphenyl pyrylium (toluene as the solvent and BF_3OEt_2 as the reactant) we obtained a low yield of 18%. During the studies on modifying the synthetic procedure, we discovered the reaction to proceed in a solvent-free medium. Thus, we carried out optimization studies to both increase the yield and obtain the pyrylium compound in a solvent-free medium. As a result of these studies, the yield of triphenylpyrylium was increased by up to 47% under optimized solvent-free conditions (Table 1).

Table 1. Optimization conditions for the solventless synthesis of 2,4,6-triphenylpyrylium.

Entry	Benzaldeyde (equiv.)	Acetophenone (equiv.)	$BF_3(OEt)_2$ (equiv.)	Temperature (°C)	Yield %
1	1	2	2.5	50	22
2	1	2	2.5	120	37
3	1	2	5	120	24
4	**1**	**3**	**2.5**	**120**	**47**
5	1	4	2.5	120	39
6	1	3	1.2	120	37

In the procedure we developed, 1 equiv. of corresponding benzaldehyde and 3 equiv. of acetophenone were heated at 120°C for 1 hour in the presence of 2.5 equiv. of $BF_3(OEt)_2$. Then the crude material was dissolved in acetone, precipitated by adding ether, and washed with acetone-ether (1:2). Using this procedure, compounds **1-6** with different substituents on phenyl groups were synthesized in 23-58% yields (Figure 1). **3**, **4** and **6** have been synthesized for the first time in this study.

Characterization of the synthesized compounds was carried out by ^{1}H and ^{13}C NMR techniques. For **5**, mass spectroscopic analysis was also performed. The ^{1}H NMR spectrum of this compound is given in Figure 2 as an example. All proton signals of this compound are expected to shift to the higher field, due to the electron-donating properties of N, N-dimethyl amino, and methyl groups. Protons that are in the same ring with the auxochomes were observed to be affected by these groups. The **d** and **e** protons on the methyl-bearing ring resonated at 8.24 and 7.48 ppm, respectively, splitting each other's signals into a doublet (J = 8.2 Hz). The **a** and **b** protons signal on the other phenyl ring were observed at 8.4 and 6.88 ppm, respectively (J = 9.3 Hz). The chemical shifts of the protons on the pyryllium nucleus were particularly interesting. In 2,4,6-triphenyl pyryllium, the signals of the protons on the pyrylium core are at 9.19 ppm, while this value has shifted up to 8.5 ppm (**c**) for **5**. This finding indicates that the pyryllium core is in strong electronic communication with the phenyl rings attached to it. The protons of the N,N-dimethylamino group and the methyl groups directly attached to the phenyl gave peaks at 3.21 and 2.46 ppm, respectively. When mass spectroscopic analysis (ESI) of **5** was performed in positive mode, the molecule was seen to ionize by the loss of the counter ion BF_4^-. The difference between the calculated (380.2009) and found (380.2031) mass values for the compound was 5.8 ppm.



	R1	R2	R3	R4	Yield%
1	H	H	H	H	47
2	$N(Me)_2$	H	H	H	55
3	$N(Me)_2$	OH	H	H	23
4	$N(Me)_2$	OMe	H	H	61
5	$N(Me)_2$	H	H	Me	16
6	OMe	OMe	OMe	H	43

Figure 1. The synthesized pyrylium compounds and the reaction yields.

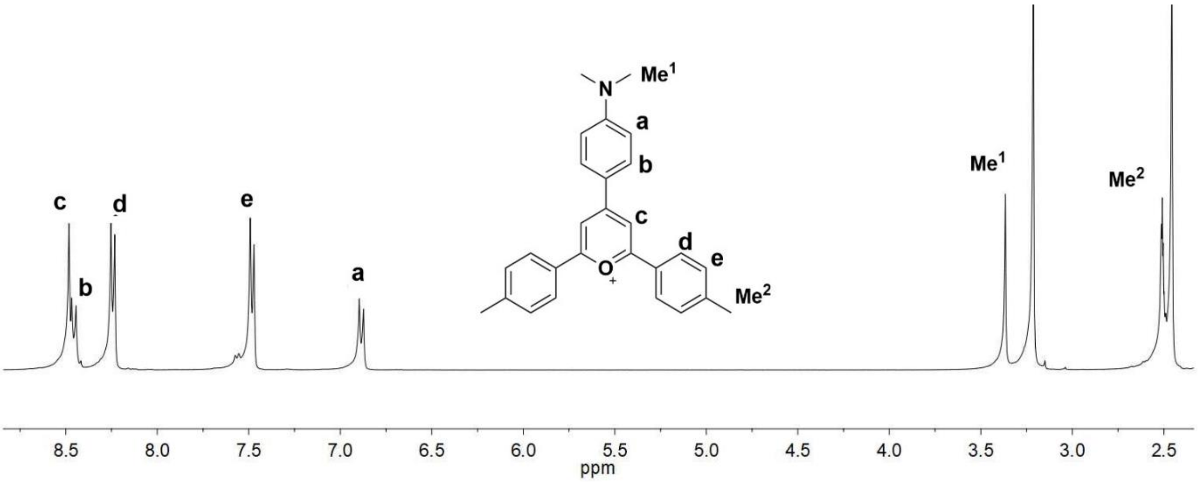


Figure 2. ^{1}H NMR spectrum of **5** in d-DMSO. The peaks at 3.33 and 2.5 belong to water and d-DMSO, respectively (Fulmer et al., 2010).

3.2 Photophysical studies

In the next step, the photophysical properties of the solutions of **1**-**6** in acetonitrile were investigated. The obtained absorption and fluorescence spectra of the compound are given in Figure 3 and the measured values are summarized in Table 2. The lowest energy absorption band of **1** was observed to be at 404 nm in this solution. This compound fluoresces at 465 nm with a 68% fluorescence quantum yield when excited at this wavelength. When the photophysical properties of compound **2** were examined, it was seen that the dimethyl amino group on 4-phenyl had dramatic effects on the photophysical properties. This substituent shifted the absorption wavelength to 536 nm and increased the molar absorption coefficient of the compound up to 4 times compared to compound **1**. The compound also be observed to be non-fluorescent. The dramatic bathochromic shift (132 nm), the increase in the molar absorption coefficient, and the quenching of the strong fluorescence altogether can be explained by an intramolecular charge transfer (ICT) process; There should be a strong excited state intramolecular charge transfer between the positively-charged pyrylium core and the electron-donor N,N-dimethylamino group.

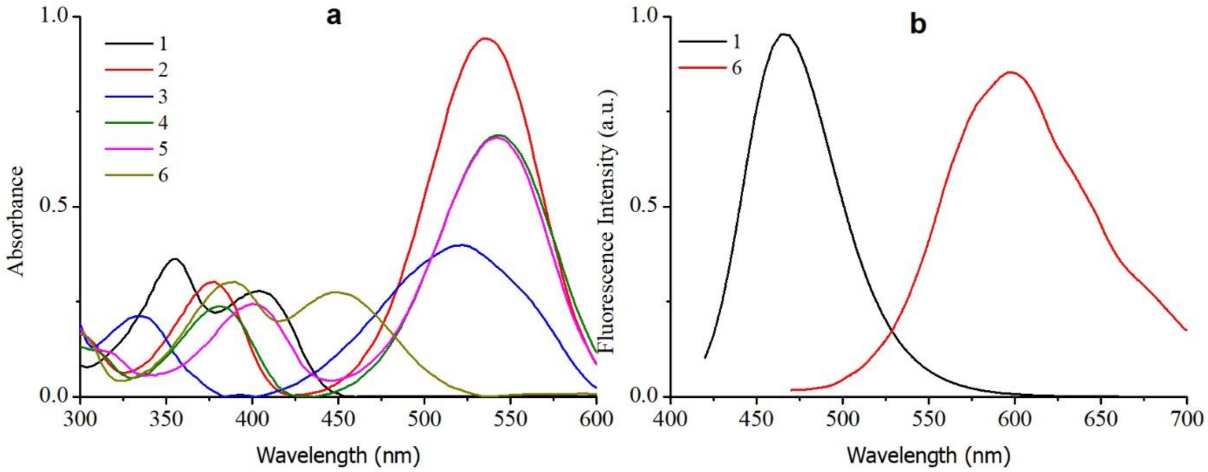


Figure 3. (**a**) Absorption and (**b**) fluorescence spectra of **1-6** in acetonitrile. The fluorescence intensities are not to be compared.

Table 2. Photophysical data for the pyrylium compounds **1-6** in acetonitrile.

Compound	**λ_{abs} (nm)**	**$\lambda_{flo, max}$ (nm)**	**Stokes shift (nm)**	**log(ε)**	**ϕ_f**
1	404	465	61	4.45	0.68
2	535	-	-	4.99	-
3	524	-	-	4.68	-
4	543	-	-	4.91	-
5	543	-	-	4.91	-
6	451	598	148	4.45	>0.0

When the photophysical properties of compounds **3** and **4** were examined, the hydroxyl and methoxy substituents were seen to cause 11 nm hypsochromic and 8 nm bathochromic shifts, respectively. Although the molar absorption coefficients of both compounds are lower compared to **2**, this difference is up to 2 times for **3**. In the first place, it could be thought that the hydroxyl group would increase the charge separation in the ICT process with its electron donor property. However, these observations indicate the presence of another interaction/process in the compound. One possible explanation may be the stabilization of the ground state through intermolecular hydrogen bonding between hydroxyl hydrogens and amine nitrogens.

The absorption spectrum of compound **5** completely overlaps with that of compound **4** at their lowest energy regions. Apparently, two methyl groups at positions 2 and 6 cause the same auxochromic effects as methoxy at position 4. The absorption spectra of compounds differ only in their π-π* transition wavelengths (ca. 40 nm).

When the photophysical properties of **6** were examined, the three methoxy groups on the 2-phenyl were observed to cause a 47 nm bathochromic shift in the absorption wavelength when compared to **1**. This compound also fluoresces although it has a very low quantum yield (>0.01). Considering the changes in the photophysical changes, there also exists a distinct ICT although not as pronounced as in the N,N-dimethylamino-substituted pyryliums.

4. Conclusion

In conclusion, we have synthesized six pyrylium compounds three of which have not been previously reported. We first carried out optimization studies on the classical synthetic procedure. Upon these studies we have shown that the pyrylium compounds can be synthesized in the absence of a solvent with increased yields When the photophysical properties of the synthesized compounds were examined, the strong auxochrome properties of N, N-dimethylamine were manifested on the pyrylium core. In the presence of this auxochrome, the effects of methoxy and hydroxy substituents on photophysical properties were seen to become less pronounced.

Author contribution

Synthesis, structure characterization, photophysical studies.

Declaration of ethical code

The author of this article declares that the materials and methods used in this study do not require ethical committee approval and/or legal-specific permission.

Conflicts of interest

The author declares that there is no conflict of interest.

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