

Synthesis of 2,5-diphenyl-3,4-distyrylcyclopenta-2,4-dienone

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Summary: A series of 2,5-diphenyl-3,4-distyrylcyclopenta-2,4-dienone (**3a-i**) and 2,5-diphenyl-3,4-bis((1E,3E)-4-phenylbuta-1,3-dienyl)cyclopenta-2,4-dienone (**5**) have been synthesized by the condensation of various (1E,5E)-1,[-diarylhexa-1,5-diene-3,4-dione (**1a-i**) and (1E,3E,7E,9E)-1,10-diphenyldeca-1,3,7,9-tetraene-5,6-dione (**4**) with 1,3-diphenylpropan-2-one (**2**) using sodium hydride in dichloromethane. Electronic absorption and emission spectral studies have shown an efficient π -interaction due to the extended conjugation in the cyclopentadienones (**3a-i**, **5**). The electronic excitation in the near UV-region (250-390 nm) to strong emission near (500-690 nm), allowing these to consider as light-harvesting species.

Keywords: Cinnamils, Cyclopentadienones, Electronic spectra.

Introduction

Tetracyclones are the compounds in which four aryl groups are attached to a cyclopentadienone core [1]. The cyclopentadienone core is anti-aromatic as indicated by the valence bond depiction (Fig-1) [2].

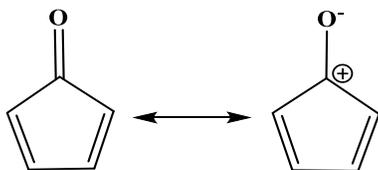


Fig. 1: Cyclopentadienone and its anti-aromatic valence bond (VB) structure.

The incorporation of the aryl moieties on the cyclopentadienone core endure steric hindrance and as a result stability to such type of systems [3]. Tetracyclones are emerged as an interesting molecule due to their functionalizable structural features and diverse applications. They are valuable repeating units for (low HOMO-LUMO band gap) conjugated oligopolymers and polymers [4-5]. These gaps can be tuned with the substituents (electron releasing or electron withdrawing) on the phenyl rings. Due to their photophysical properties, some industrial applications are related to them for their use as emissive or absorbing materials for LEDs. Organic materials have been extensively applied in light emitting diodes due to their versatility and color-tunability [6-16]. In 2000 Heeger *et al.*, won a Nobel prize in Chemistry for their study on organic conductive materials and fabrication

of OLED (organic light emitting diodes) [17]. Cyclopentadienones, in particular, are also synthetic precursors of phenylenes [18] which are target materials for the similar applications. To improve fluorescence and film-forming properties of the tetracyclones, their intrinsic electrical, optical, and morphological properties can be tuned by modifying the peripheral aryl groups *i.e.* insertion of extended conjugation (olefinic moieties) between aryl groups and cyclopentadienone core.

Experimental

All solvents and reagents were obtained from commercial sources. Dichloromethane (CH_2Cl_2) was dried over CaH_2 and freshly distilled before used. Methanol (MeOH) was dried with Mg/I_2 , distilled and was kept over molecular sieves. Nitrogen was purged through distilled solvents and reagents to deoxygenate wherever necessary. $^1\text{H-NMR}$ was recorded at 500 MHz, on a Bruker DRX 500 NMR spectrometer. All $^1\text{H-NMR}$ spectra were taken at 25 °C in the deuterated solvents. The progress of the reaction was tracked by analytical thin-layer chromatography using silica gel pre-coated plates (E. Merck). Compounds were envisioned by 254 nm light and with iodine. Flash column chromatography was carried out to purify the product by using flash silica gel from Silicycle (60 Å, 40-63 μm) with the eluent. The purity of the products was checked by the combination of Thin-layer chromatography (TLC), and Gel permeation chromatography (GPC), (LC-MS) Liquid

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chromatography-mass spectrometry (Mass spectrometry facility, University of Pennsylvania). Either protonated molecular ions $[M+H]^+$ or $[M-H]^+$ or sodium adducts $[M+Na]^+$ were used for empirical formula confirmation. The cinnamils (1E,5E)-1,6-diarylhexa-1,5-diene-3,4-dione (**1a-i**) and (1E,3E,7E,9E)-1,10-diphenyldeca-1,3,7,9-tetraene-5,6-dione (**4**) were synthesized using the reported procedure [19-29].

Synthesis of 2,5-diphenyl-3,4-distyrylcyclopenta-2,4-dienone (3a-i, 5)

General procedure

1,3-diphenylpropan-2-one (0.1 mol) was added to a solution of cinnamils (1E,5E)-1,6-diarylhexa-1,5-diene-3,4-dione (**1a-i**) and (1E,3E,7E,9E)-1,10-diphenyldeca-1,3,7,9-tetraene-5,6-dione (**4**) (0.1 mol) dissolved in dry dichloromethane (100 mL). Sodium hydride (0.2 mol) was added as a base and the reaction mixture was stirred at 35 °C for 24 hours. Completion of the reaction was tracked by TLC and ¹H-NMR. The reaction contents were diluted with dichloromethane (50 mL) and washed with saturated solution of ammonium chloride. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered and evaporated. The compound was purified by silica gel column chromatography (EtOAc: hexanes, 3:1). After drying under high vacuum, the solid compound was obtained.

2,5-Diphenyl-3,4-distyrylcyclopenta-2,4-dienone (3a)

A yellow solid M.P. = 180 °C. Yield 90%; ¹H NMR (500 MHz, CDCl₃) δ 6.62 - 7.39 (m, 24 H); ¹³C NMR (126 MHz, CDCl₃) δ 126.41, 127.48, 128.04, 128.34, 128.54, 129.35, 130.54, 130.66, 131.12, 140.63, 140.66, 143.03; IR (neat) 3027, 1715, 1462, 762 cm⁻¹; UV-VIS; λ_{max} (CH₂Cl₂/nm) = 230, 360 nm; LC-MS_{ES-} (*m/z*): $[M-H]^+$ = 435.21.

3,4-Bis(4-fluorostyryl)-2,5-diphenylcyclopenta-2,4-dienone (3b)

A yellowish brown solid M.P. = 182 °C. Yield 85%; ¹H NMR (500 MHz, CDCl₃) δ 6.16 - 7.41 (m, 22 H); IR (neat) 3026, 1700, 1508, 685 cm⁻¹; UV-VIS; λ_{max} (CH₂Cl₂/nm) = 240, 330 nm; LC-MS_{ES+} (*m/z*): $[M+H]^+$ = 473.13.

3,4-Bis(4-chlorostyryl)-2,5-diphenylcyclopenta-2,4-dienone (3c)

A yellow solid M.P. = 185 °C. Yield 85%; ¹H NMR (500 MHz, CDCl₃) δ 6.90 - 7.96 (m, 22 H); IR

(neat), 3026, 1706, 1582, 760 cm⁻¹; UV-VIS; λ_{max} (CH₂Cl₂/nm) = 235, 320 nm; LC-MS_{ES+} (*m/z*): $[M+Na]^+$ = 527.13, $[M+2+Na]^+$ = 529.13.

3,4-Bis(4-bromostyryl)-2,5-diphenylcyclopenta-2,4-dienone (3d)

A yellow solid M.P. = 190 °C. Yield 86%; ¹H NMR (500 MHz, CDCl₃) δ 6.90 - 7.98 (m, 22 H); IR (neat) 3026, 1706, 1452, 760 cm⁻¹; UV-VIS; λ_{max} (CH₂Cl₂/nm) = 235, 420 nm; LC-MS_{ES+} (*m/z*): $[M+H]^+$ = 595.13, $[M+2+H]^+$ = 597.17.

3,4-Bis(4-methoxystyryl)-2,5-diphenylcyclopenta-2,4-dienone (3e)

A yellow solid M.P. = 183 °C. Yield 89%; ¹H NMR (500 MHz, CDCl₃) δ 6.70 - 7.96 (m, 22 H), 3.78 (s, 6H, 2 OCH₃); IR (neat) 2988, 1758, 1507, 790 cm⁻¹; UV-VIS; λ_{max} (CH₂Cl₂/nm) = 255, 385 nm; LC-MS_{ES+} (*m/z*): $[M+H]^+$ = 497.13.

3,4-Bis(4-methylstyryl)-2,5-diphenylcyclopenta-2,4-dienone (3f)

A yellow solid M.P. = 185 °C. Yield 87%; ¹H NMR (500 MHz, CDCl₃) δ 6.70 - 7.96 (m, 22 H), 2.33 (s, 6H, 2CH₃); IR (neat) 3026, 1706, 1452, 760 cm⁻¹; UV-VIS; λ_{max} (CH₂Cl₂/nm) = 245, 370 nm; LC-MS_{ES+} (*m/z*): $[M+H]^+$ = 465.13.

3,4-Bis(4-(dimethylamino)styryl)-2,5-diphenylcyclopenta-2,4-dienone (3g)

A solid M.P. = 260 °C. Yield 80%; ¹H NMR (500 MHz, CDCl₃) δ 6.10 - 7.96 (m, 22 H), 3.05 (s, 12 H, 4CH₃); IR (neat) 3000, 1508, 1452, 704 cm⁻¹; UV-VIS; λ_{max} (CH₂Cl₂/nm) = 250, 390 nm; LC-MS_{ES-} (*m/z*): $[M-H]^-$ = 521.28.

3,4-Bis(4-(diethylamino)styryl)-2,5-diphenylcyclopenta-2,4-dienone (3h)

A yellow solid M.P. = 280 °C. Yield 80%; ¹H NMR (500 MHz, CDCl₃) δ 6.90 - 8.10 (m, 22 H), 1.3 (6H dd, *J* = 6.1 Hz), 4.2 (4H, dt, *J* = 6.9 Hz); IR (neat) 3026, 1706, 1452, 760 cm⁻¹; UV-VIS λ_{max} (CH₂Cl₂/nm) = 235 nm; LC-MS_{ES+} (*m/z*): $[M+H]^+$ = 579.13.

3,4-Bis(4-nitrostyryl)-2,5-diphenylcyclopenta-2,4-dienone (3i)

A yellow solid M.P. = 280 °C. Yield 78%; ¹H NMR (500 MHz, CDCl₃) δ 6.50 - 7.99 (m, 22 H); IR

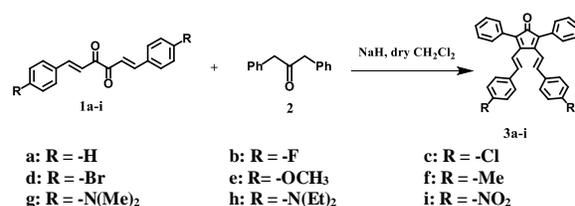
(neat) 2935, 1596, 1518, 702 cm^{-1} ; UV-VIS; λ_{max} ($\text{CH}_2\text{Cl}_2/\text{nm}$) = 235, 275 nm; LC-MS ES^+ (m/z): $[\text{M}+\text{Na}]^+ = 549.54$.

2,5-Diphenyl-3,4-bis((1E,3E)-4-phenylbuta-1,3-dienyl)cyclopenta-2,4-dienone (**5**)

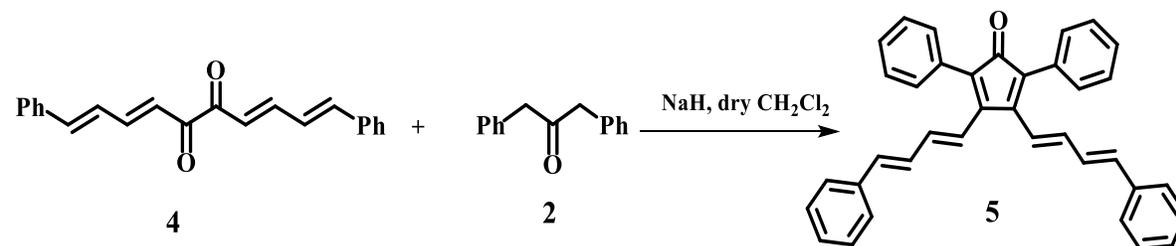
A yellow solid M.P. = 190 $^\circ\text{C}$. Yield 88%; ^1H NMR (500 MHz, CDCl_3) δ 6.90 - 8.26 (m, 28 H); IR (neat) 3026, 1706, 1452, 760 cm^{-1} ; UV-VIS; λ_{max} ($\text{CH}_2\text{Cl}_2/\text{nm}$) = 240, 365 nm; LC-MS ES^+ (m/z): $[\text{M}+\text{H}]^+ = 489.20$.

Result and Discussion

The most common method reported in the literature for the synthesis of tetracyclones involves the condensation of 1,2-diarylethane-1,3-dione with 1,3-diarylaceton using potassium hydroxide as a base in ethanol at reflux [30-35]. In the present work, a modified procedure has been used for the condensation of cinnamils (1E,5E)-1,6-diarylhexa-1,5-diene-3,4-dione (**1a-i**) and (1E,3E,7E,9E)-1,10-diphenyldeca-1,3,7,9-tetraene-5,6-dione (**4**) with 1,3-diphenylpropan-2-one (**2**) using sodium hydride as a base in dichloromethane on stirring at 35 $^\circ\text{C}$ to obtain 2,5-diphenyl-3,4-distyrylcyclopenta-2,4-dienone (**3a-i**) [Scheme 1] and 2,5-diphenyl-3,4-bis((1E,3E)-4-phenylbuta-1,3-dienyl)cyclopenta-2,4-dienone (**5**) [Scheme 2]. The yields of the synthesized compounds were excellent and the newly developed method was found to be superior than classical method involving potassium hydroxide which was unsuccessful in the present work.



Scheme-1: Synthesis of 2,5-diphenyl-3,4-distyrylcyclopenta-2,4-dienone (**3a-i**).



Scheme-2: Synthesis of 2,5-diphenyl-3,4-bis((1E,3E)-4-phenylbuta-1,3-dienyl)cyclopenta-2,4-dienone (**5**)

The synthetic compounds were characterized by ^1H -NMR, LC-MS, IR spectral studies. In ^1H -NMRs, the specific signals for aromatic and olefinic proton were appeared as unrevealed multiplets in the region of δ 6.50 - 7.90 probably due to the occurrence of conformational mixture. However, the shifting of signals attributed to various aromatic and olefinic protons by changing the substituents (-F, -Cl, -Br, -OCH₃, -NO₂, -N(Me)₂, -N(Et)₂, -Me) on the phenyl ring was observed. Methoxy protons in 3,4-bis(4-methoxystyryl)-2,5-diphenylcyclopenta-2,4-dienone (**3e**) were appeared at δ 3.86. Methyl protons in 3,4-bis(4-methylstyryl)-2,5-diphenylcyclopenta-2,4-dienone (**3f**) can be seen at δ 2.40. In 3,4-bis(4-(dimethylamino)styryl)-2,5-diphenylcyclopenta-2,4-dienone (**3g**), methyl protons appeared at δ 3.05 and for 3,4-bis(4-(diethylamino)styryl)-2,5-diphenylcyclopenta-2,4-dienone (**3h**), the methyl protons were observed at δ 1.26 and methylene protons at δ 4.20. LC-MS spectra taken in dichloromethane in both modes ES^{+1} and ES^{-1} confirmed the formation of the compounds. The functional groups present in the compounds were noted by infrared spectra *i.e.* the appearance of bands at 3026 cm^{-1} (C=C) and 1706 cm^{-1} (C=O).

Optical Studies

The optical properties of some of the compounds were investigated by UV-visible absorption and photoluminescence (PL) spectral studies. Fig. 2 shows the UV-vis spectra in CH_2Cl_2 at concentration 0.01 mM. All the cyclopentadienones (**3a-i**, **5**) exhibited two electronic transitions, designated as $\lambda_{1\text{max}}$ and $\lambda_{2\text{max}}$. Table-1 summarizes the absorption wavelength and the corresponding molar extinction coefficient which was determined by linear regression of the data using Beer's law. The $\lambda_{1\text{max}}$ can be accounted for the π - π^* transition and the higher $\lambda_{2\text{max}}$ for n - π^* excitation. Substitution with electron donating groups on phenylethenyl moieties led to bathochromic shift and with electron withdrawing groups led to hypsochromic shift of both π - π^* and n - π^* transitions, as expected. Table-2 summarizes photo-physical properties of compounds **3a**, **3e**, **3f**, **3g**, and **5**.

Table-1: UV-Spectral data for 2,5-diphenyl-3,4-distyrylcyclopenta-2,4-dienone.

Compound	λ^1_{nm}	ϵ	λ^2_{nm}	ϵ
3a	230	22670	360	1600
3b	235	23670	320	1590
3d	255	23670	385	1848
3e	245	23670	370	1718
3f	250	23670	390	1809
3i	230	15670	275	1550
5	240	23700	365	1582

Table-2: Photo Physical Properties.

Compound	λ (absorption)nm	λ (Emission)nm
3a	230	507
3e	245, 385	523, 568, 616
3f	285, 375	525, 568, 618
3g	235, 390	569, 620
5	240	523

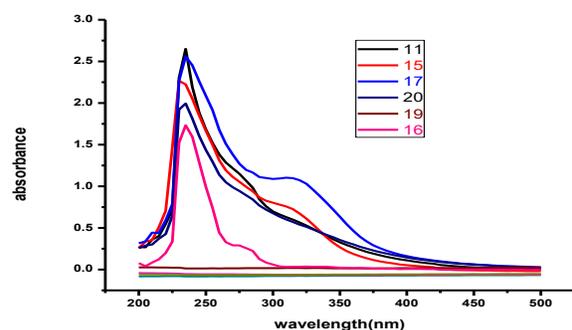


Fig. 2: Combined UV-spectra for 2,5-diphenyl-3,4-distyrylcyclopenta-2,4-dienone (3a=11, 3e=15, 3f=16, 3g=17, 3i=19 and 5=20).

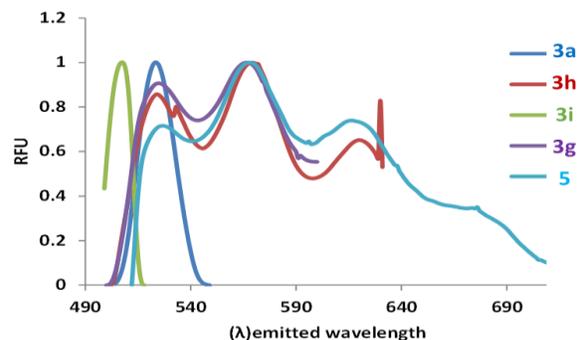


Fig. 3: Combined emission spectra for 2,5-diphenyl-3,4-distyrylcyclopenta-2,4-dienone (3a, 3g, 3h, 3i, 5).

In the PL spectra (Fig. 3) each compound (3a, 3g, 3h, 3i, 5) exhibited an emission maximum in the 500-690 nm region. The emission spectrum of (5) showed the maximum at 690 nm which was red-shifted compared to others. Therefore, the skeleton affords more effective π -electron delocalization over the entire 18 π electron system leading to the red-shifted absorption. Electron absorption and emission spectral studies have shown an efficient π -interaction

of the highly conjugated framework in the cyclopentadienones under investigations.

Conclusion

In this study, a series of 2,5-diphenyl-3,4-distyrylcyclopenta-2,4-dienone (3a-i) and 2,5-diphenyl-3,4-bis((1E,3E)-4-phenylbuta-1,3-dienyl)cyclopenta-2,4-dienone (5) have been synthesized by the condensation of cinnamils (1E,5E)-1,6-diarylhexa-1,5-diene-3,4-dione (1a-i) and (1E,3E,7E,9E)-1,10-diphenyldeca-1,3,7,9-tetraene-5,6-dione (4) with 1,3-diphenylpropan-2-one (2) using sodium hydride in dichloromethane in excellent yields. The synthetic compounds have shown good photo-physical properties. To the best of our knowledge, such type of cyclopentadienones has not been reported in the literature.

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