Rapid Communication

Substituent directed distal photoisomerisation of >C=C< in indolic dienyl chromophores

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Methyl-3-methyl-5-(3-*N*-benzenesulphonylindole)-2*E*,4*E*-penta-dienoate and methyl-3-methyl-5-(3-*N*-H indole)-2*E*,4*E*-penta-dienoate are synthesized and their photoisomerisation behaviour in 1,4-dioxane and methanol are examined. The photoiso-merisation of these compounds is highly dependent upon the substituent present at the indolic nitrogen atom.

Light-induced geometrical isomerisation of carbon-carbon double bond (>C=C<) of linear polyenes plays a crucial role in many photobiological processes[1,2]. It is also considered important in materials and nanoelectronics[3,4]. Consequently, the excited state properties of ethenes, dienes, trienes and related linear polyenes have been extensively examined and reviewed[5-17]. The geometrical photoisomerisation of >C=C< in these molecules is influenced by the substituent and solvent polarity. Linear polyenes particularly can exhibit regiospecific photoisomerisation and dipolar excited states are believed to be involved in their photoisomerisation process. Various mechanistic models including one-bond-flip (OBF)[18], bicycle-pedal (BP)[19] and Hula-twist (HT)[20] have been proposed for the observed photoisomerisations. However, several questions remain unanswered about the structure and dynamics of the excited state involved in these photoisomerisations. The regiospecificity and the polarity of the excited state can be examined by studying the photoisomerisation of appropriate model compounds. Earlier, the photoisomerisation of α,ω-diphenylpolyenes has been examined and the relevance of dipolar excited states in the photoprocesses of linear polyenes discussed[21,22]. Herein are reported studies on the effect of substituent and solvent polarity on the photoisomerisation of dienyl indoles *viz.* methyl-3-methyl-5-(3-*N*-benzene-sulphonylindole)-2*E*,4*E*-pentadienoate, **1** and methyl-3-methyl-5-(3-N-H indole)-2*E*,4*E*-pentadienoate, **2** (**Figure 1**).

Results and Discussion

Direct irradiation of a solution of **1** (2*E*,4*E*) gives a photomixture consisting of 2*E*,4*E* and 2*Z*,4*E* isomers. Similarly, direct irradiation of **2** (2*E*,4*E*) in solution yields a photomixture consisting of 2*E*,4*E* isomer along with 2*Z*,4*E*, 2*E*,4*Z* and 2*Z*,4*Z* isomers. The photoisomerisation quantum yields (Φ_{PI}) and photo-stationary state compositions (PSS) are given in **Table I**. The ^{1}H NMR spectra of **1** and its photomixture are shown in **Figures 2a** and **2b**. Thus, while in the case of **1**, the trisubstituted double bond selectively undergoes *trans-cis* photoisomerisation, in the case of **2** both the double bonds photoisomerise (**Figure 3**). From the conversion plot (**Figure 4**), it is seen that **2** gives only two isomers (2*Z*,4*E* and 2*E*,4*E*) within a period of 20 min. However, the other two isomers (*viz.* 2*E*,4*Z* and 2*Z*,4*Z*) appear only after 20 min of irradiation. Thus, these isomers do not appear to be formed from initial 2*E*,4*E*. It is suggested that the energy required for *trans-cis* isomerisation for the trisubstituted double bond is lower as compared to the other double bonds.

The photoisomerisation of the trisubstituted double bond (>C=C< double bond away from the indolyl ring) occurs selectively, both in non-polar as well as in polar solvents. The PSS composition is largely insensitive to solvent polarity. However, it is highly sensitive to the substituent present at the indolic-N. The observed photoisomerisation patterns can be explained in terms of relative reaction volume requirement for the twisting of various >C=C<. The >C=C< in **1** near the indolic unit requires relatively more reaction volume due to the presence of bulky -$SO_2C_6H_5$ substituent, and hence resists isomerisation. Thus, while the isomerisation of **1** yields only one isomer (2*Z*,4*E*), isomerisation of **2** yields three isomers (2*Z*,4*E*), (2*E*,4*Z*) and (2*Z*,4*Z*). This work provides a new factor that can be involved in distally controlling the photoisomerisation of linear polyenes of biological and materials significance.
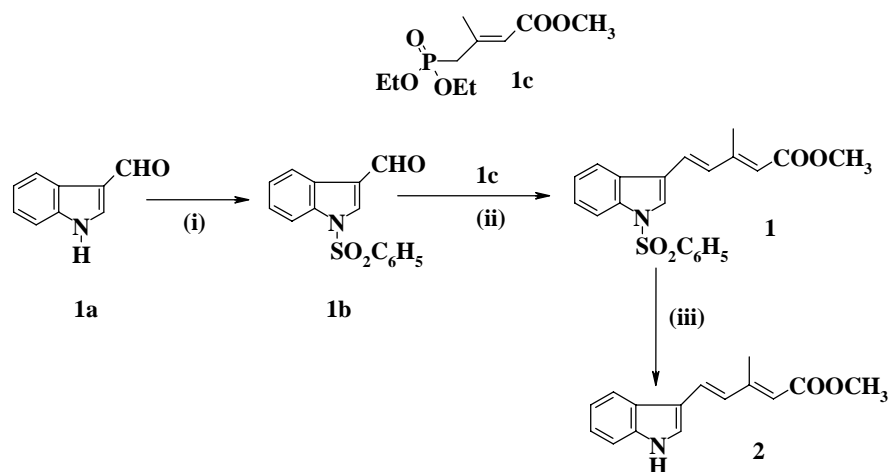
Figure 1 — Synthesis of methyl-3-methyl-5-(3-*N*-benzenesulphonylindole)-2*E*,4*E*-pentadienoate, **1** and methyl-3-methyl-5-(3-*N*-H indole)-2*E*,4*E*-pentadienoate, **2**. Reagents and conditions: (i) C6H5SO2Cl, K2CO3, acetone, RT, 3 h. (ii) NaH, THF, 0°C, 2 h. (iii) aq. NaOH, ethanol, 25°C, 24 h

Table I — PSS composition and Φ_{PI} for **1** and **2**

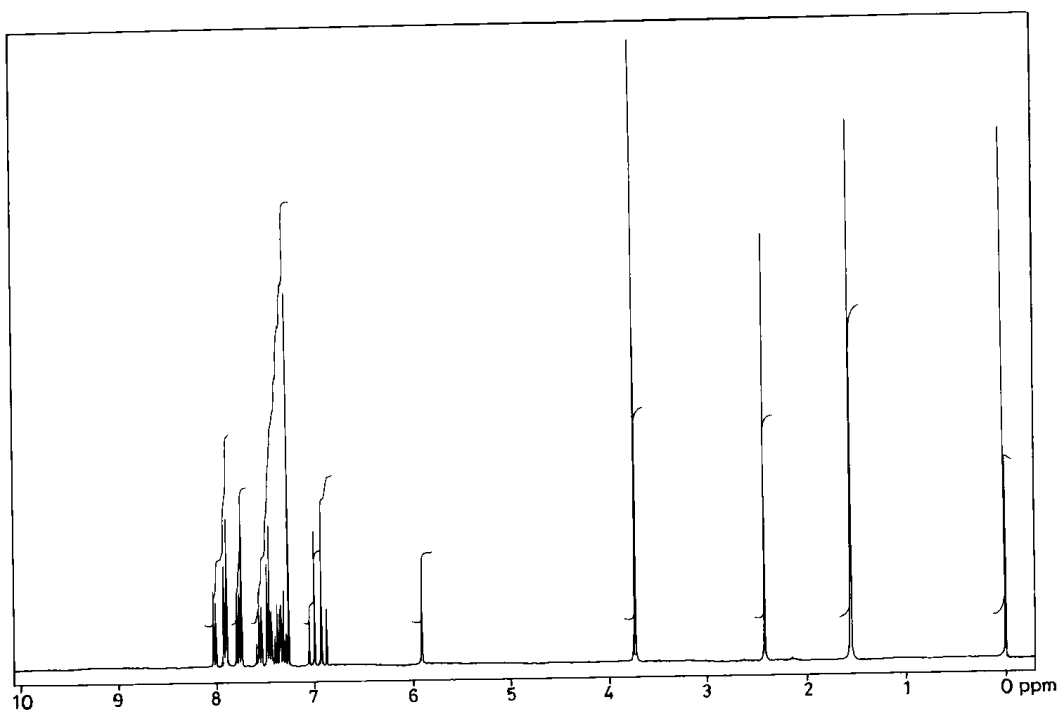| Starting Compd	Solvent	% PSS composition				Φ_{PI}
		2*E*,4*E*	2*Z*,4*E*	2*E*,4*Z*	2*Z*,4*Z*	
1 (2*E*,4*E*)	1,4-Dioxane	83	17	0	0	0.02
	Methanol	82	18	0	0	0.03
2 (2*E*,4*E*)	1,4-Dioxane	34	47	10	9	0.05
	Methanol	38	29	17	16	0.08

Figure 2a — ^{1}H NMR (300 MHz, CDCl3) spectrum **1**
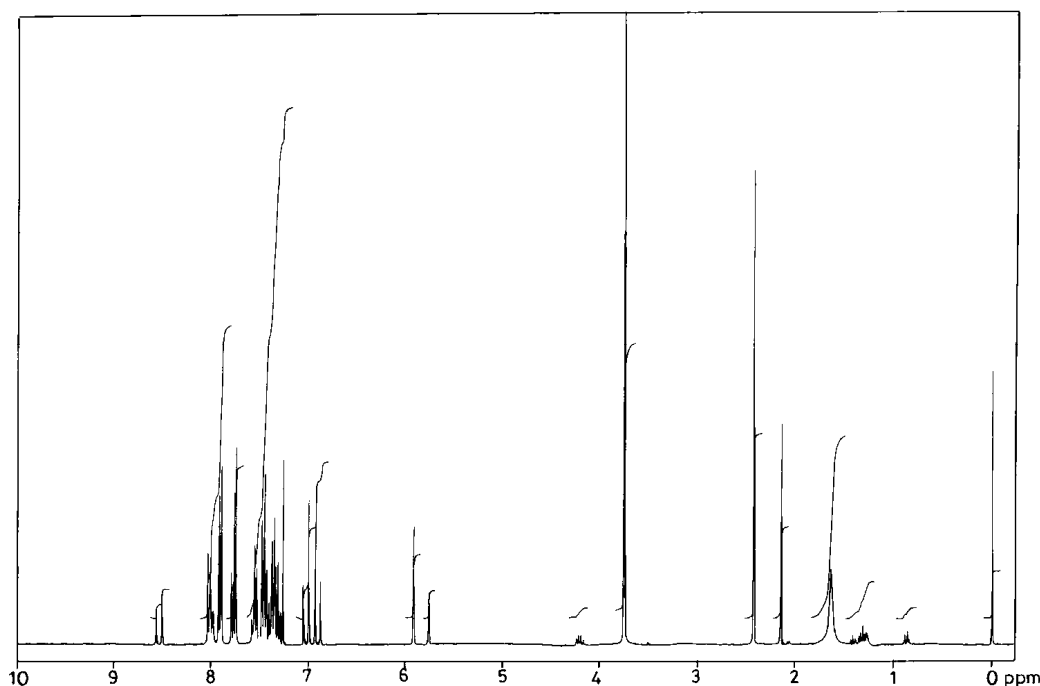
Figure 2b — ^{1}H NMR (300 MHz, CDCl$_3$) spectrum of photomixture of **1**
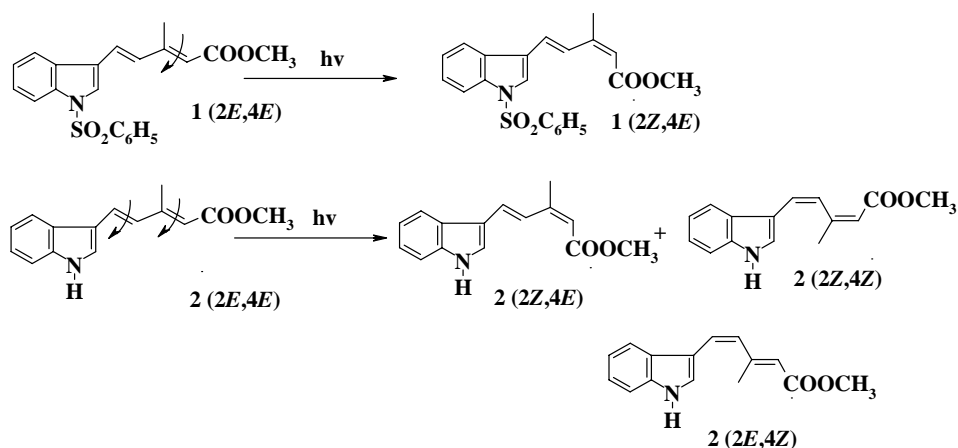

Figure 3 — Photoisomerisation of **1** and **2**

Experimental Section

Absorption spectra were measured on Shimadzu UV-160A spectrophotometer and JASCO-V-570 UV-Vis/IR spectrophotometer. FTIR spectra in KBr disc were recorded on Impact Nicolet-400 spectrophotometer. ^{1}H NMR spectra in CDCl$_3$ as solvent and TMS as an internal standard were recorded on a Varian 300 MHz FTNMR spectrometer. Mass spectra were recorded by employing electro spray ionization (QT, YA-105, Micro mass, Waters). HPLC analyses were carried out on a Hitachi L6250 intelligent pump fitted with

Hitachi U-2000 Spectrophotometer. Melting points were determined on a Veego melting point apparatus and are uncorrected.

3-Formyl indole, **1a,** other reagents for the synthesis and AR grade solvents were procured from the local suppliers. 3-Formyl-*N*-benzenesulphonyl indole, **1b** was prepared in 89% yield by reacting **1a** (taken in potassium carbonate in acetone) with benzene sulphonyl chloride in a manner similar to the literature procedure[23]. m.p. 155-57°C (Lit.[23] m.p. 157-58°C).
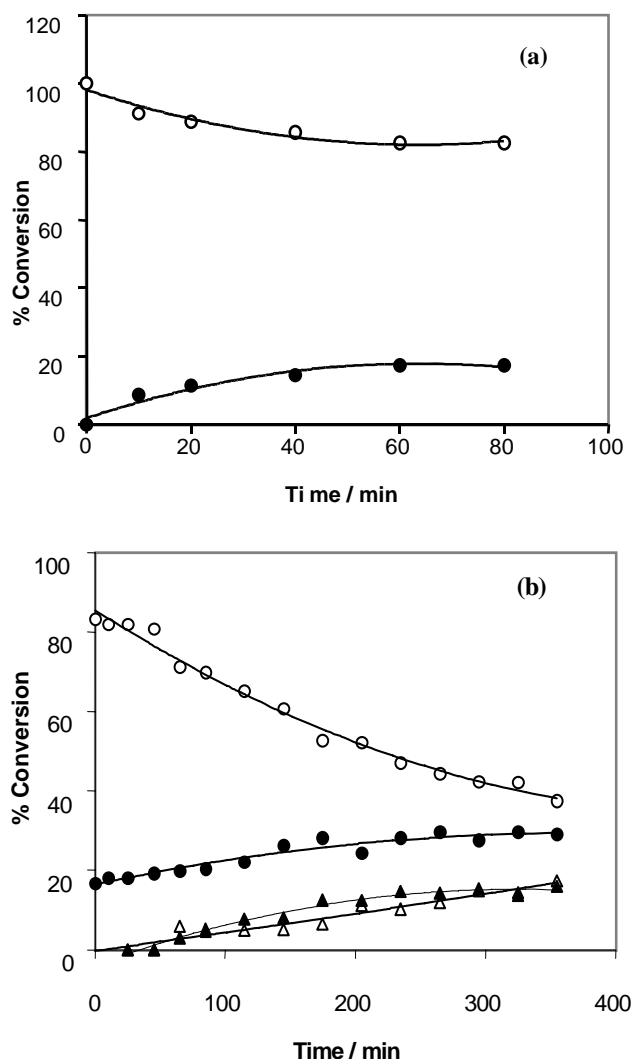
Figure 4 — Action plots showing % disappearance (2*E*,4*E*) (o) and formation of photoproducts (2*Z*,4*E*) (•), (2*E*,4*Z*) (Δ) and (2*Z*,4*Z*) (▲) for **1** (a) and for **2** (b) in methanol

Methyl-3-methyl-5-(3-*N*-benzenesulphonyl indole)-2*E*,4*E*-penta-dienoate, 1

A solution of phosphonate, methyl-4-(diethyl phosphono)-3-methyl-2-butenoate (**1c**, 2.3 g, 6.5 mmol in 10 mL of THF), prepared by following the literature procedure[24], was added to sodium hydride (0.78 g, 32.5 mmole) suspension in THF. The reaction mixture was kept at 0°C under crushed ice-bath. The mixture was stirred under the flow of dry nitrogen atmosphere until the colour of the reaction mixture turned gradually from dark yellow to orange. A solution of **1b** (0.45 g, 1.6 mmole) in 20 mL of dry THF was dropwise added to the reaction mixture over a period of 30 min and stirring was continued at 0°C for about 3 h. The reaction mixture was quenched by addition of crushed ice and the product was extracted

with diethyl ether. The crude product was isolated after removal of solvent under reduced pressure. The crude product was subjected to column chromatography (5% ethyl acetate in petroleum ether), when the desired pure compound was obtained in 16% yield. m.p. 144-45°C; HPLC R_t = 6.4 min (Lichrosorb Si-60, 5 μ, 250 mm × 4.6 mm, ethyl acetate-hexane 1:9, 2 mL/min, 358 nm); UV-Vis (MeOH): λ_{max} nm (ε, 1 mol^{-1}cm^{-1}) 328 (32500); IR (KBr): 1713 (-COOCH$_3$), 1607 (C=C), 1146 cm^{-1} (S=O); ^{1}H NMR (CDCl$_3$): δ 2.42 (3H, s, -CH$_3$), 3.74 (3H, s, -COOCH$_3$), 5.91 [1H, s, -C(CH$_3$)=CH-], 6.90 (1H, d, *J* = 16 Hz, indole-C=CH-), 7.02 (1H, d, *J* = 16 Hz, indole–CH=C–), 7.25-7.41 (2H, m, -C$_5$-H and -C$_6$-H), 7.45-7.58 (3H, m, -benzene-away from sulphonyl-H), 7.74-7.78 (2H, m, -benzene-near sulphonyl-H), 7.88-7.92 (2H, m, -C$_4$-H, and -C$_7$-H), 8.01 (1H, m, -C$_2$-H); TOF MS: ES$^+$ for C$_{21}$H$_{19}$NSO$_4$ Calcd: 381.111 (M$^+$), Found: 382.111 (MH$^+$).

Methyl-3-methyl-5-(3-N-H-indole)-2*E*, 4*E*-pentadienoate, 2

A mixture of **1** (50 mg, 2.0 × 10^{-4} mole) in 10 mL of ethanol and sodium hydroxide solution (5 mL, 20% aq. NaOH) was stirred at 25°C for 24 h. The alkaline reaction mixture was neutralised with 2*N* hydrochloric acid and the crude product was extracted with diethyl ether solvent. The organic solvent was removed under reduced pressure and the crude product was purified by column chromatograph using 10% ethyl acetate-petroleum ether mixture as eluting solvent, when the desired compound was obtained in 80% yield. m.p. 104-06°C; HPLC R_t = 16.5 min (Lichrosorb Si-60, 5 μ, 250 mm × 4.6 mm, ethyl acetate-hexane 1:9, flow rate 2 mL/min, detector wavelength 358 nm); UV-Vis (MeOH): λ_{max} nm (ε, 1 mol^{-1}cm^{-1}) 359 (26666); IR (KBr): 3471 (-NH), 1698 (-COOCH$_3$), 1605 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$): δ 2.45 (3H, s, -CH$_3$), 3.76 (3H, s, -COOCH$_3$), 5.88 [1H, s, -C(CH$_3$)=CH-], 6.90 (1H, d, *J* = 16 Hz, indole-C=CH-), 7.20 (1H, d, *J* = 16 Hz, indole -CH=C-), 7.37-7.44 (2H, m, -C$_5$-H and -C$_6$-H), 7.90-7.93 (2H, m, -C$_4$-H, and -C$_7$-H), 8.10 (1H, m, -C$_2$-H); TOF MS: ES$^+$ for C$_{15}$H$_{15}$NO$_2$ Calcd: 241.118 (M$^+$), Found: 242.118 (MH$^+$).

For photoisomerisation, solution of **1** and **2** were irradiated with a 400 W medium pressure mercury lamp. The desired irradiation wavelength was isolated by a monochromator. Photoisomerisation quantum yield (Φ_{PI}) was determined against potassium ferrioxalate actinometer[25]. Irradiated solutions were

analysed by UV-Vis and ^{1}H NMR. Analytical data for the photomixture of **1** (data corresponding to product 2*Z*,4*E* is underlined). UV-Vis (methanol, λ_{max}): 328 nm**.** HPLC (10% ethyl acetate in hexane, flow rate 2.0 mL /min, detection wavelength 365 nm): R_t 6.4 min (2*E*,4*E*), R_t 5.95 min (2*Z*,4*E*); ^{1}H NMR (CDCl$_3$): δ 2.14 (3H, s, -CH$_3$), 2.42 (3H, s, -CH$_3$), 3.75 (3H, s, -COOCH$_3$), 3.74 (3H, s, -COOCH$_3$), 5.75 [1H, s, -C(CH$_3$)=CH-], 5.91 [1H, s, -C(CH$_3$)=CH-], 6.90 (1H, d, *J* = 16 Hz, indole-C=CH-), 7.01 (1H, d, *J* = 16.84 Hz, indole-C=CH-), 7.02 (1H, d, *J* = 16 Hz, indole-CH=C-), 7.25-7.41 (2H, m, -C$_5$-H and -C$_6$-H), 7.45-7.58 (3H, m, -benzene-away from sulphonyl-H), 7.74-7.78 (2H, m, -benzene-near sulphonyl-H), 7.88-7.92 (2H, m, -C$_4$-H, and -C$_7$-H), 8.01 (1H, m, -C$_2$-H), 8.52 (1H, d, *J* = 16.84 Hz, indole-CH=C-). Analytical data for the photomixture of **2** (data corresponding to products are underlined). UV-Vis (methanol, λ_{max}): 358 nm**,** HPLC (10% ethyl acetate in *n*-hexane, flow rate 2.0 mL /min), detection wavelength, λ = 365 nm, R_t = 11.36 min (2*Z*,4*Z*), R_t = 12.46 min (2*E*,4*Z*), R_t = 15.98 min (2*Z*,4*E*), R_t = 16.53 min (2*E*,4*E*). ^{1}H NMR (CDCl$_3$): δ 2.16 (3H, s, -CH$_3$), 2.45 (3H, s, -CH$_3$), 3.70 (3H, s, -COOCH$_3$), 3.71 (3H, s, -COOCH$_3$), 3.73 (3H, s, -COOCH$_3$), 3.76 (3H, s, -COOCH$_3$), 5.25 [1H, s, -C(CH$_3$)=CH-], 5.66 [1H, s, -C(CH$_3$)=CH-], 5.80 [1H, s, -C(CH$_3$)=CH-], 5.87 [1H, s, -C(CH$_3$)=CH-], 6.88 (1H, d, *J* = 16 Hz, indole-C=CH-), 7.18 (1H, d, *J* = 16 Hz, indole-CH=C-), 7.20-7.27 (m, -C$_5$-H and –C$_6$-H), 7.36-7.40 (m, -C$_4$-H, and –C$_7$-H), 7.90-7.92 (m), 8.08-8.10 (m), 8.41 (1H, b, s, -NH), 8.46 (s), 8.51 (s).

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