

The effects of 3,5-substitutions on the photochromism and photoisomerization of some 2,3,4,4,5,6-hexasubstituted 4H-thiopyrans

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Abstract

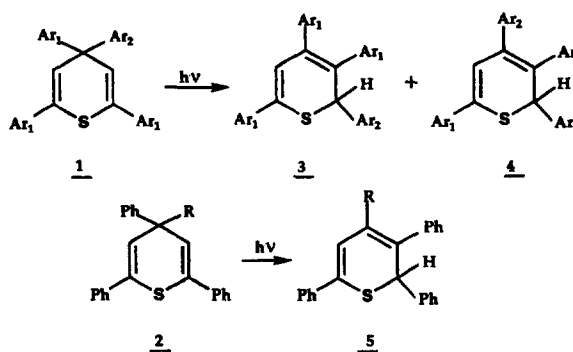
Some new derivatives of 4-aryl- and 4-methyl-2,3,4,5,6-pentaphenyl-4H-thiopyrans (**6a–6d**) and 4-aryl- and 4-methyl-2,4,6-triphenyl-3,5-dimethyl-4H-thiopyrans (**7a–7d**) were synthesized, and their photochromism and photoisomerization reactions were compared with those of 2,4,4,6-tetraphenyl-4H-thiopyran (**1a**) ($Ar_1 \equiv Ar_2 \equiv Ph$) and 2,4,6-triphenyl-4-methyl-4H-thiopyran (**2a**) ($R \equiv Me$) model compounds having no substituents at the 3,5-positions. The results show that, unlike the photochromic model compound **1**, the 3,5-diphenyl-substituted 4H-thiopyrans **6a–6c**, on exposure to sunlight or UV radiation in the solid state, do not exhibit any photochromic properties, whereas photochromic behaviour is retained in the 3,5-dimethyl-substituted 4H-thiopyran analogues **7a–7c** with a blue shift in the absorption in the visible region. Moreover, on irradiation of **6a–6c** with UV light in methanol or benzene solution, no photoisomerization to isomeric 2H-thiopyrans is detected, whereas the 3,5-dimethyl-substituted 4H-thiopyrans **7a–7d**, as well as the 3,5-diphenyl analogue **6d**, give the isomeric 2H-thiopyrans **10**, **11** and **9d** respectively with relative yields lower than the corresponding model compounds **1a** and **2a**.

Keywords: Photochromism; Photoisomerization; 4H-Thiopyran derivatives

1. Introduction

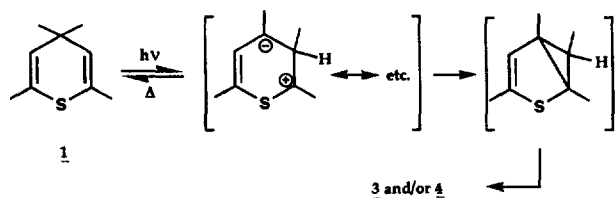
Recently, the reversible photocolouration and photoisomerization properties of 2,4,4,6-tetrasubstituted 4H-thiopyrans have been the subject of studies in our and other laboratories [1–7]. It is known that the 3,5-unsubstituted 2,4,4,6-tetraaryl-4H-thiopyrans **1**, unlike the 2,4,6-triphenyl-4-alkyl-4H-thiopyrans **2**, undergo a thermally reversible photochemical colour change in the solid state on illumination with UV radiation or sunlight. On repeated illumination, the initially formed coloured species of **1**, with absorption maxima in the visible region at 540–660 nm, as well as the crystalline non-photochromic 4H-thiopyrans **2**, partially rearrange to the corresponding isomeric 2H-thiopyrans **3**, **4** and **5** with low yields via irreversible fatigue processes [1,2,6,7].

Compounds **1** and **2** do not exhibit any photocolouration changes in polar or non-polar solvents; however, the same photoisomerizations occur in solution to form the 2H-thiopyrans **3**, **4** and **5** in nearly quantitative yields, with no alkyl group rearrangement [1]. Although a non-photochromic bicyclic intermediate has been trapped from the reaction mixture in solution and converted to its isomeric 2H-thiopyran [6,7], the structure of the photocoloured species and the

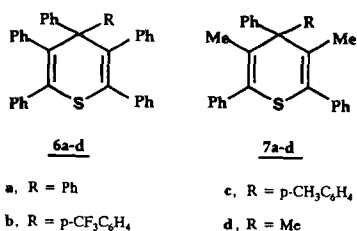


mechanisms of photochromism and photoisomerization in 4H-thiopyran systems are still open to debate and experimental studies are required [4,6,7]. On the basis of the spectroscopic and kinetic properties of the thermal bleaching process of the intense coloured species in the solid state, the effects of solvent polarity and the trapping and conversion of a bicyclic intermediate in solution, the following scheme has been postulated for the whole photochemical reaction pathway with respect to the unimolecular nature of the process [7].

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Considering the sterically hindered structures involved in the reaction pathway, it seemed of considerable importance to examine the effects of 3,5-substitutions on the inhibition of the photoproducts because of the extensive steric crowding in some 2,3,4,4,5,6-hexasubstituted 4H-thiopyrans. Accordingly, new hexasubstituted 4-aryl-2,3,4,5,6-pentaphenyl-4H-thiopyrans (**6a–6c**), 2,3,4,5,6-pentaphenyl-4-methyl-4H-thiopyran (**6d**), 4-aryl-2,4,6-triphenyl-3,5-dimethyl-4H-thiopyrans (**7a–7c**) and 2,4,6-triphenyl-3,4,5-trimethyl-4H-thiopyran (**7d**) were selected for synthesis and study.



2. Experimental details

Melting points (m.p.) were taken on a Gallenkamp melting point apparatus and are uncorrected. UV and visible spectra were determined with a Shimadzu UV-2100 or a Shimadzu 265-FW spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded with a Varian EM 390 or a Bruker AC-80 spectrometer, and mass spectra with a Finnigan MAT-TSQ 70 mass spectrometer at an ionizing voltage of 70 eV. Analyses were performed on a Heraeus CHNO Rapid instrument. All photolyses were carried out using a low-pressure mercury lamp equipped with a special quartz tube to give a wavelength of 254 nm. The NMR chemical shifts are reported on the δ scale in parts per million downfield from internally added tetramethylsilane.

2.1. Syntheses

The new hexasubstituted 4H-thiopyrans **6a–6d** and **7a–7d** were synthesized from reactions of organolithium or organomagnesium salts with 2,3,4,5,6-pentaphenylthiopyrylium perchlorate (the corresponding pyrylium salt was prepared by the method of Simalty and Carretto [8]; conversion of the pyrylium salt to the desired thiopyrylium was accomplished by the procedure previously described for the preparation of other analogues by Wizinger and Ulrich [9]) and 2,4,6-

triphenyl-3,5-dimethylthiopyrylium perchlorate [10] respectively, according to the methods reported in Ref. [11], and were purified by recrystallization from alcohol in nearly 20%–70% yields. In some cases, the 2H-thiopyran isomers were also formed in the reaction mixture and were separated by fractional recrystallization or identified in solution.

2.1.1. 2,3,4,4,5,6-Hexasubstituted 4H-thiopyran (**6a**)

Colourless crystals, m.p. 273–275 °C (from iso-AmOH). m/z 554 (M^+ 50.10%), 477 (16.36), 178 (52.72), 166 (100), 121 (30.90), 77 (18.63). UV λ_{max} (*n*-BuOH) nm (log ϵ): 232 (4.46), 282 (4.29). ¹H NMR (C₆D₆) δ : 6.50–7.65 (m, ArH). Analysis: calculated for C₄₁H₃₀S: C, 88.77; H, 5.41; found: C, 88.30; H, 5.40.

2.1.2. 4-(*p*-Trifluoromethylphenyl)-2,3,4,5,6-pentaphenyl-4H-thiopyran (**6b**)

Colourless crystals, m.p. 240–242 °C (from EtOH). m/z 622 (M^+ 100%), 477 (13.63), 454 (29.10), 178 (36.36), 166 (50.91), 77 (9.10). UV λ_{max} (*n*-BuOH) nm (log ϵ): 231 (4.57), 278 (4.43). ¹H NMR (C₆D₆) δ : 6.19–7.21 (m, ArH). ¹³C NMR (C₆D₆) δ : 65.65 (C-4), 98.29 (CF₃), 124.05, 126.63, 127.01, 127.53, 128.27, 128.50, 129.45, 131.66, 132.32, 132.99, 137.24, 137.96, 139.29, 140.49, 144.32, 149.47. ¹⁹F NMR (C₆D₆) δ : 90.87 (CF₃). Analysis: calculated for C₄₂H₂₉F₃S: C, 81.00; H, 4.69; found: C, 81.07; H, 4.57.

2.1.3. 4-(*p*-Tolyl)-2,3,4,5,6-pentaphenyl-4H-thiopyran (**6c**)

Colourless crystals, m.p. 263–265 °C (from *n*-BuOH). m/z 569 (M^+ 31.81%), 554 (100), 477 (22.91), 178 (59.09), 166 (78.26), 121 (18.18), 77 (40.45). UV λ_{max} (*n*-BuOH) nm (log ϵ): 230 (4.58), 281 (4.42). ¹H NMR (C₆D₆) δ : 2.06 (3H, s, Me), 6.63–7.66 (29H, m, ArH). Analysis: calculated for C₄₂H₃₂S: C, 88.69; H, 5.67; found: C, 88.60; H, 5.57.

2.1.4. 2,3,4,5,6-Pentaphenyl-4-methyl-4H-thiopyran (**6d**)

¹H NMR (C₆D₆) δ : 1.95 (3H, s, Me), 6.87–7.65 (25H, m, ArH).

2.1.5. 2,4,4,6-Tetraphenyl-3,5-dimethyl-4H-thiopyran (**7a**)

Colourless crystals, m.p. 128–129 °C (from EtOH). m/z 430 (M^+ 31.00%), 415 (44.00), 353 (100.00), 121 (12.10), 77 (7.90). UV λ_{max} (CHCl₃) nm (log ϵ): 243 (4.36). ¹H NMR (CDCl₃) δ : 1.36 (6H, s, 2Me), 7.24–7.67 (20H, m, ArH).

2.1.6. 4-(*p*-Trifluoromethylphenyl)-2,4,6-triphenyl-3,5-dimethyl-4H-thiopyran (**7b**)

Colourless crystals, m.p. 135–136 °C (from EtOH). m/z 498 (M^+ 54.60%), 483 (98.40), 421 (100.00), 353 (57.10), 165 (20.40), 121 (19.50), 77 (15.40). UV λ_{max} (CHCl₃) nm (log ϵ): 242 (4.27). ¹H NMR (CDCl₃) δ : 1.35 (6H, s, 2Me), 6.69–7.69 (19H, m, ArH).

2.1.7. 4-(*p*-Tolyl)-2,4,6-triphenyl-3,5-dimethyl-4H-thiopyran (**7c**)

Colourless crystals, m.p. 160–161 °C (from EtOH). *m/z* 444 (M^+ 61.70%), 429 (98.90), 367 (100.00), 353 (79.60), 165 (35.30), 121 (16.80), 91 (11.80), 77 (11.60). UV λ_{\max} (CHCl₃) nm (log ϵ): 242 (4.26). ¹H NMR (CDCl₃) δ : 1.36 (6H, s, 2Me), 2.38 (3H, s, Me), 6.96–7.80 (19H, m, ArH).

2.1.8. 2,4,6-Triphenyl-3,4,5-trimethyl-4H-thiopyran (**7d**)

Colourless crystals, m.p. 105–106 °C (from EtOH). *m/z* 368 (M^+ 5.00%), 353 (27.00), 291 (37.00), 202 (15.00), 165 (22.00), 121 (100.00), 77 (67.00). UV λ_{\max} (CHCl₃) nm (log ϵ): 244 (4.33). ¹H NMR (C₆D₆) δ : 1.46 (6H, s, Me-3, Me-5), 1.76 (3H, s, Me-4), 7.07–7.38 (15H, m, ArH).

2.1.9. 2-(*p*-Tolyl)-2,3,4,5,6-pentaphenyl-2H-thiopyran (**8c**)

Yellow crystals, m.p. 179–180 °C (from *n*-BuOH). *m/z* 569 (M^+ 76.36%), 445 (100.00), 368 (30.91). UV λ_{\max} (*n*-BuOH) nm (log ϵ): 255 (4.55), 370 (3.72), characteristic for 2H-thiopyran system. ¹H NMR (C₆D₆) δ : 2.00 (3H, s, Me), 6.66–7.53 (29H, m, ArH). ¹³C NMR (C₆D₆) δ : 20.96 (Me), 74.13 (C-2), 126.66, 126.94, 127.43, 127.52, 128.00, 128.21, 128.69, 129.09, 130.17, 130.60, 136.16, 136.40, 138.44, 139.33, 144.10, 147.91. Analysis: calculated for C₄₂H₃₂S: C, 88.69; H, 5.67; found: C, 88.10; H, 5.46.

2.2. General irradiation procedures

The photochemical irradiations of 4H-thiopyrans **6a–6d** and **7a–7d** in methanol or benzene solution were carried out either in a 60 mm × 372 mm quartz tube as described earlier [1] or in a sealed pyrex NMR tube under an argon atmosphere; irradiation was performed using a monochromatic low-pressure mercury lamp with $\lambda = 254$ nm at room temperature. The progress of all photochemical reactions were monitored by ¹H NMR and/or UV spectroscopy.

2.3. Photoproducts

In a typical photolysis experiment, when the product was present at a suitable concentration irradiation was stopped. The photoproduct was either identified in solution or characterized by preparative thin layer chromatography (PTLC) on alumina using ether–petroleum ether (10 : 90) as eluent followed by recrystallization from alcohol. The structures assigned to the photoproducts rest on their spectral data in accord with the expected behaviour of the 2H-thiopyran system [1,6,7]. The yields were determined by ¹H NMR spectroscopy.

2.3.1. 2,2,3,5,6-Pentaphenyl-4-methyl-2H-thiopyran (**9d**)

¹H NMR (C₆D₆) δ : 2.00 (3H, s, Me), 6.87–7.65 (25H, m, ArH).

2.3.2. 2,3,4,6-Tetraphenyl-2,5-dimethyl-2H-thiopyran (**10a**)

Yellow crystals, m.p. 165–166 °C (from EtOH). *m/z* 430 (M^+ 87.57%), 415 (97.00), 353 (100.00), 121 (72.19), 103 (75.74). UV λ_{\max} (CHCl₃) nm (log ϵ): 242 (4.29), 343 (3.85). ¹H NMR (CDCl₃) δ : 1.51 (3H, s, Me-2), 1.60 (3H, s, Me-5), 6.80–7.90 (20H, m, ArH).

2.3.3. 2-(*p*-Trifluoromethylphenyl)-3,4,6-triphenyl-2,5-dimethyl-2H-thiopyran (**10b**) and 4-(*p*-trifluoromethylphenyl)-2,3,6-triphenyl-2,5-dimethyl-2H-thiopyran (**11b**)

¹H NMR (CDCl₃) δ : 1.49 and 1.51 (3H, two singlets, Me-2), 1.59 (3H, broad singlet, Me-5), 7.00–8.10 (19H, m, ArH).

2.3.4. 2-(*p*-Tolyl)-3,4,6-triphenyl-2,5-dimethyl-2H-thiopyran (**10c**) and 4-(*p*-tolyl)-2,3,6-triphenyl-2,5-dimethyl-2H-thiopyran (**11c**)

¹H NMR (CDCl₃) δ : 1.49 and 1.51 (3H, two singlets, Me-2), 1.57 (3H, broad singlet, Me-5), 2.24 (3H, s, Me), 6.80–7.90 (19H, m, ArH).

2.3.5. 2,3,6-Triphenyl-2,4,5-trimethyl-2H-thiopyran (**11d**)

¹H NMR (C₆D₆) δ : 1.54 (3H, s, Me-2), 1.77 (3H, s, Me-4), 1.83 (3H, s, Me-5), 7.07–7.38 (15H, m, ArH).

3. Results and discussion

3.1. Photochromism

The 2,3,4,4,5,6-hexaaryl-substituted 4H-thiopyrans **6a–6c**, in contrast with the 2,4,4,6-tetraaryl-substituted 4H-thiopyran analogues **1** [4–8], on exposure to sunlight or UV radiation in the solid state, do not exhibit any thermally reversible photocolouration. This dramatic change reveals that substitution of phenyl groups at the 3,5-positions of tetraaryl-substituted 4H-thiopyrans alters the photocolouration behaviour of the system. However, in the 2,4,4,6-tetraaryl-3,5-dimethyl-substituted 4H-thiopyrans **7a–7c**, the photocolouration changes are restored; crystals change from colourless to violet in a few minutes on irradiation with sunlight or UV radiation. The violet colour gradually fades in the dark, and the thermally reversible colour changes can be repeated for an indefinite number of cycles. The reflection spectra of the coloured crystals, recorded in the visible region for a mixture of **7a–7c** and MgO (1 : 3) using MgO as a standard, exhibit broad absorption bands around 540 nm. A comparison between the observed wavelengths of the model compound **1a** (Ar₁ ≡ Ar₂ ≡ Ph) and those of the 4H-thiopyrans **7a–7c** (Table 1) shows that introduction of dimethyl substituents at the 3,5-positions leads to hypsochromic shifts in the absorption maxima.

2,3,4,5,6-Pentaphenyl-4-methyl-4H-thiopyran **6d** and 2,4,6-triphenyl-3,4,5-trimethyl-4H-thiopyran **7d**, in accord with the non-photochromic 2,4,6-triphenyl-4-alkyl-4H-thio-

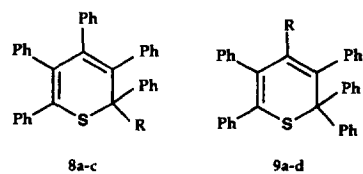
Table 1
Maximum absorption wavelengths of the coloured species for 4H-thiopyrans **1a** and **7a–7c** in the visible region

λ_{\max} (nm)	1a	7a	7b	7c
	575	550	530	540

pyran analogues **2**, remain colourless on exposure to sunlight or UV radiation in the solid state. Also, like the model compound **1**, none of the non-photochromic 4H-thiopyrans **6a–6c** or photochromic 4H-thiopyrans **7a–7c** exhibit any reversible photochemical colour changes in benzene solution.

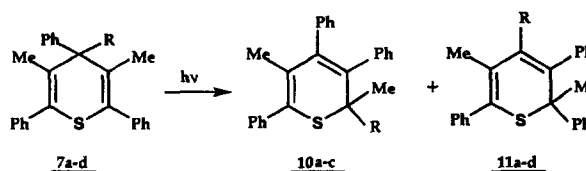
3.2. Photoisomerization

In order to study the effects of 3,5-substitutions on the photoisomerization of 2,3,4,4,5,6-hexasubstituted 4H-thiopyrans, photolyses of compounds **6a–6d** and **7a–7d** were carried out in methanol and/or benzene solution, and the results were compared with those of the corresponding analogous model compounds **1a** and **2a** under identical experimental conditions; the variations in the characteristic UV absorption around 370 nm for the 2H-thiopyran system and/or the ^1H NMR spectra were recorded on repeated irradiation. On irradiation of 6×10^{-4} M colourless solutions of **6a–6c** in benzene with UV light ($\lambda = 254$ nm) under an argon atmosphere in a quartz tube at room temperature for 20 min, no absorption bands around 370 nm, characteristic of the expected isomeric 2H-thiopyrans **8a–8c** or **9a–9c**, are detected, whereas in the case of a colourless solution of the model compound **1a** a new band appears around 370 nm, and after the same irradiation time 2H-thiopyran **3a** is formed in about 50% yield. This behaviour of 2,3,4,4,5,6-hexaaryl-4H-thiopyrans **6a–6c** contrasts sharply with that of the 3,5-unsubstituted model compound **1a** and, as observed during solid state illumination, reveals an effect originating from steric interactions between the phenyl substituents. It should be noted that the expected photoproducts **8a–8c** or **9a–9c** are thermodynamically stable compounds, since during the course of the synthesis of **6c** from 2,3,4,5,6-pentaphenylthiopyrylium perchlorate and *p*-tolyllithium salt, the yellow crystalline 2H-thiopyran **8c** with a UV absorption band at 370 nm (Fig. 1) was separated and characterized from the reaction mixture.



On irradiation of a 6×10^{-4} M colourless solution of 3,5-dimethyl-substituted 4H-thiopyran **7a** in methanol with UV light ($\lambda = 254$ nm) under argon in a quartz tube at room temperature for 20 min, the signal of the 3,5-dimethyl groups

in the ^1H NMR spectrum at $\delta = 1.36$ decreases with the appearance of two singlets at 1.51 (Me-2) and 1.60 (Me-5). The photoproduct was isolated as yellow crystals and identified as 2,3,4,6-tetraphenyl-2,5-dimethyl-2H-thiopyran **10a** on the basis of similarities in the UV (Fig. 2) and ^1H NMR spectra with those of compounds **3** and **4**. Irradiation of the separately prepared 6×10^{-4} M solutions of **7b** and **7c** in methanol, by analogy with the photochemical reactions in 4H-thiopyrans **1**, gives mixtures of both aryl-migrated products **10b**, **10c** and **11b**, **11c**.



In the ^1H NMR spectra, the signals of the methyl groups at the 3,5-positions of **7b** and **7c** at $\delta \approx 1.35$ decrease, while two new sharp singlets appear at $\delta = 1.49$ and 1.51 (2Me-2) with a broad singlet at $\delta \approx 1.58$ (2Me-5). The yields of the photorearranged products of **7a–7c** and **1a** were determined by ^1H NMR using the ratios of the characteristic signals of 4H-thiopyran to the corresponding 2H-thiopyran isomers. The data shown in Table 2 reveal that the 3,5-dimethyl-substituted 4H-thiopyran system suffers a marked decrease in the yields of the photoproducts (**10a–10c** and **11a–11c**) with respect to that of the model compound (**3a**). The lower yields may be due to a limited steric hindrance caused by non-bonding interactions between the methyl and the phenyl groups in the system. The hypsochromic shifts (Table 1) of the absorption maxima for photochromic compounds **7a–7c**, compared with **1a**, are also in accord with this interpretation.

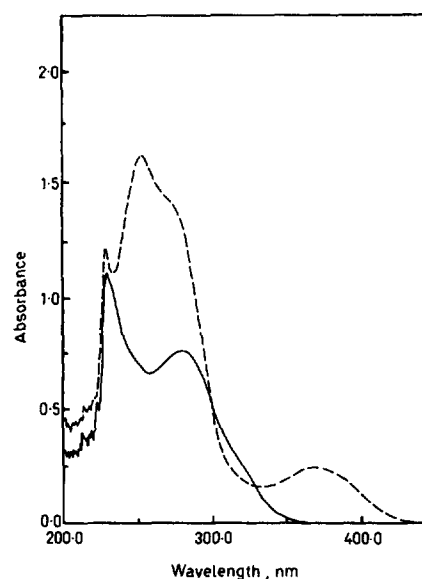


Fig. 1. UV spectra of 4H-thiopyran **6c** (—) and 2H-thiopyran **8c** (---) in *n*-BuOH.

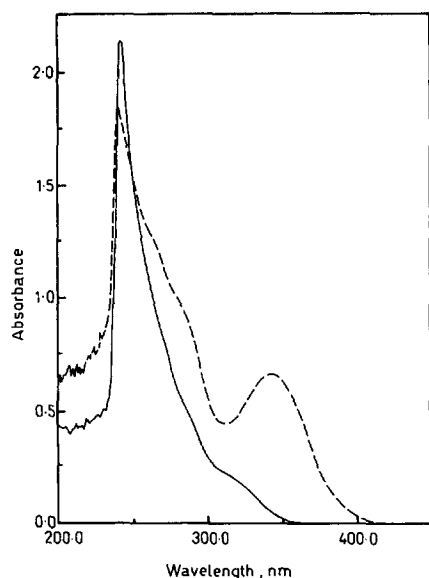


Fig. 2. UV spectra of 4H-thiopyran **7a** (—) and 2H-thiopyran **10a** (---) in CHCl_3 .

Table 2
Relative yields of the photorearranged products **3a**, **10a–10c** and **11a–11c** under identical experimental conditions

	3a	10a	10b, 11b	10c, 11c
Yield (%)	> 90	38	50	34

Table 3
Relative yields of the photorearranged products **5a**, **9d** and **11d** under identical experimental conditions

	5a	9d	11d
Yield (%)	53	32	5

Irradiation of 12×10^{-3} M solutions of the 3,5-substituted methyl analogues **6d** and **7d** in benzene- d_6 in a sealed Pyrex NMR tube under an argon atmosphere for 60 min, by analogy with the 3,5-unsubstituted model compound **2a**, gives only the phenyl-migrated products **9d** and **11d** respectively. In the ^1H NMR spectrum of **6d**, the signal of the methyl group at the 4-position at $\delta = 1.95$ is decreased, while a sharp singlet appears at $\delta = 2.00$ (Me-4). In the case of **7d**, the singlets at $\delta = 1.46$ (6H, Me-3, Me-5) and $\delta = 1.76$ (3H, Me-4) are decreased, while new singlets become visible at $\delta = 1.54$ (Me-2), $\delta = 1.77$ (Me-4) and $\delta = 1.83$ (Me-5). The relative yields shown in Table 3 reveal a marked decrease in the yields of the photoproducts **9d** and **11d** with respect to the photoproduct of the model compound (**5a**), which is in accord with steric influences.

4. Conclusions

From our investigation, it can be concluded that the substitution of phenyl groups at the 3,5-positions of tetraaryl-substituted 4H-thiopyrans alters the photochromic and photoisomerization behaviour of the system. The 3,5-dimethyl-substituted analogues show a hypsochromic shift for the photocoloured species with a marked decrease in the yield of photorearranged products. By replacement of one aryl group with a methyl group in the 4-position, the photorearranged products are formed in both cases with lower yields. These results are consistent with the operation of unfavourable steric interactions in the transition states leading to photoproducts, caused by non-bonded repulsions between the substituents of the sulphur ring which lessen the ability of the aryl groups to delocalize charges.

Acknowledgements

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