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Dyes and Pigments 49 (2001) 65–74

DYES and PIGMENTS

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Synthesis and spectroscopic properties of some merocyanine dyes

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Received 16 January 2001; accepted 1 February 2001

Dedicated to Dr. David A. Clarke on the occasion of his retirement

Abstract

The reaction between some 1,1-diarylprop-2-yn-1-ols **3** and cyclohexane-1,3-diones affords merocyanine dyes **7**, the valence tautomers of the tetrahydro-2*H*-[1]benzopyrans. The spectroscopic properties of these dyes are discussed. The isomeric merocyanine dyes **14** and **15** derived from the reaction of 1,1-bis(4-dimethyl-aminophenyl)prop-2-yn-1-ol and 2-tetralone are dehydrogenated to the photochromic 3*H*-naphtho[2,1-*b*]pyran **12**. This protocol constitutes a new route to the photochromic naphthopyran unit.

Keywords: Merocyanine dyes; Tetrahydro-2*H*-[1]benzopyrans; Valence tautomerism; 3*H*-Naphtho[2,1-*b*]pyrans; Synthesis; Photochromism

1. Introduction

There is considerable interest in the valence isomerisation of the 2*H*-pyran system, particularly the naphthologues where the valence isomerism is accompanied by a reversible change from colourless (pyran) to coloured (merocyanine) on irradiation with UV light. This phenomenon is known as photochromism and has featured in a number of reviews [1,2]. The commercial significance of the photochromism of the naphthopyrans is evident by the intense patent activity in this area [3].

The equilibrium between the 2*H*-pyran ring system **1** and the acyclic dienone isomer **2** is influenced by both electronic and steric effects and by temperature and solvent (Scheme 1) [4].

During the course of our work on photochromic naphthopyrans, [2,5] a paper detailing the reaction of some 1,1-diarylprop-2-yn-1-ols **3**, which are key intermediates for the synthesis of naphthopyrans, [1,2] with a range of acidic methylene compounds was noted (Scheme 2) [6]. The products from these reactions were identified as the merocyanine dyes **4** but no valence tautomers, pyrans **5**, were detected.

Despite the numerous examples of acidic methylene compounds utilised in this report, cyclohexane-1,3-diones were not used. The application of these cyclic diketones was of interest to us since the

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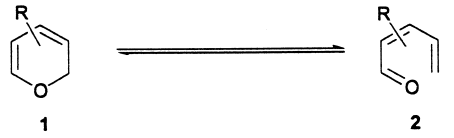
0143-7208/01/$ - see front matter
PII: S0143-7208(01)00005-5



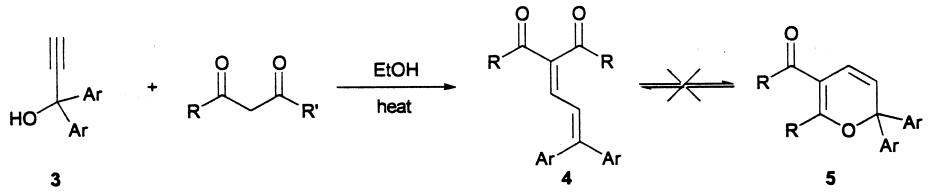
Scheme 1.

products derived from their reaction with a 1,1-diarylprop-2-yn-1-ol may exist as either the ring closed tetrahydro-2*H*-[1]benzopyran or the merocyanine dye. Simple alkyl substituted tetrahydro-2*H*-[1]benzopyrans are known and undergo valence isomerism under UV irradiation [7] and recent work has revealed that some substituted benzopyrans exhibit reversible electrocyclic ring-opening and ring-closing behaviour upon UV irradiation [8]. To our knowledge there have been no reports of either the synthesis or photochromic properties of 2,2-diaryl substituted tetrahydro-2*H*-[1]benzopyrans. Cyclohexane-1,3-diones are versatile 1,3-bifunctional building blocks in heterocyclic chemistry [9]. Of particular note is their use in the formation of 5-hydroxy-2*H*-[1]benzopyrans [10], tetrahydro-2*H*-[1]benzothiopyrans [11] and tetrahydro-9*H*-xanthen-9-ones [12]. We now report the synthesis of some novel merocyanine dyes, which are the valence tautomers of 2,2-diaryl tetrahydro-2*H*-[1]benzopyrans, using 5,5-dimethyl cyclohexane-1,3-dione (dimedone) as a key starting material.

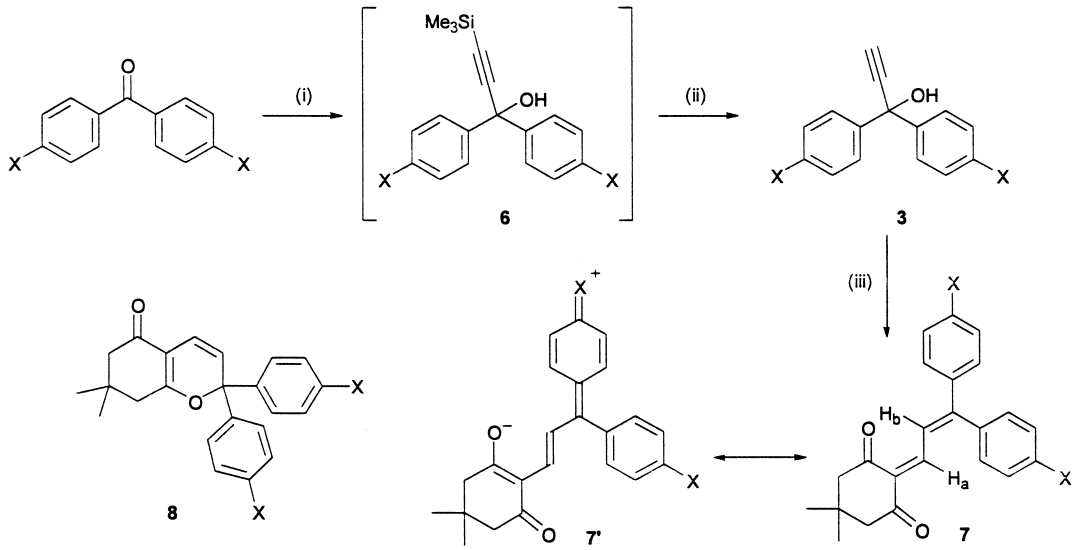
2. Results and discussion

The prop-2-yn-1-ols **3** required for the study were obtained by the addition of a suitably substituted benzophenone to trimethylsilylacetylide, derived from *n*-butyllithium and trimethylsilylacetylene, in anhydrous tetrahydrofuran (THF) under a nitrogen atmosphere (Scheme 3). The resulting adducts **6** were isolated and then desilylated using tetra-*n*-butyl ammonium fluoride (TBAF) to afford the propynols **3** as off-white solids that were sufficiently pure for further use. This two-stage protocol offers both improved yields of **3** (79–96%) and cleaner products compared with the direct use of lithium or sodium acetylide.

The addition of a catalytic quantity of 4-toluenesulfonic acid monohydrate to a stirred solution of a 1,1-bis(4-dimethylaminophenyl)prop-2-yn-1-ol **3a** and dimedone in anhydrous toluene at ca. 40°C resulted in the immediate development of an intense maroon colour (Scheme 3). TLC examination of the reaction mixture after 20 min stirring at 40°C revealed that, despite the intense colour, a significant amount of the propynol remained unreacted and thus the reaction mixture was heated to reflux until TLC revealed that no starting materials remained (ca. 30 min reflux). Removal of the solvent gave a dark red gum that solidified on addition of hexane and ethyl acetate. It was inferred from the intense colour of the product that the merocyanine **7a** had been isolated since benzopyrans are usually colourless. The key feature in the ^{1}H NMR spectrum of **7a** which confirmed the merocyanine structure was the presence of an AB system with doublets at δ 7.93 (H_b) and δ 8.27 (H_a) with a coupling constant of 12.8 Hz for the ethylene bridge protons. The ^{1}HNMR spectra of 2*H*-[1]benzopyrans also display an AB system for H-3 and H-4 with $J = 10$ Hz but these signals appear at much higher field [13]. The magnitude of the coupling constant measured for **7a** is consistent with an *s-trans* arrangement [14]. The methylene functions of **7a** are non-equivalent and appear at δ 2.46 and δ 2.51 and are shifted slightly downfield compared with the equivalent methylene functions in dimedone which resonate at ca. δ 2.2 [15]. The *geminal* methyl unit resonates at δ 1.08, whilst the



Scheme 2.



Scheme 3. Reagents: (i) lithium trimethylsilylacetylide, THF, N_2, −10°C — RT; (ii) TBAF, THF, 0°C — RT then H_3O^+; (iii) dimedone, 4-T_SOH, PhMe, heat.

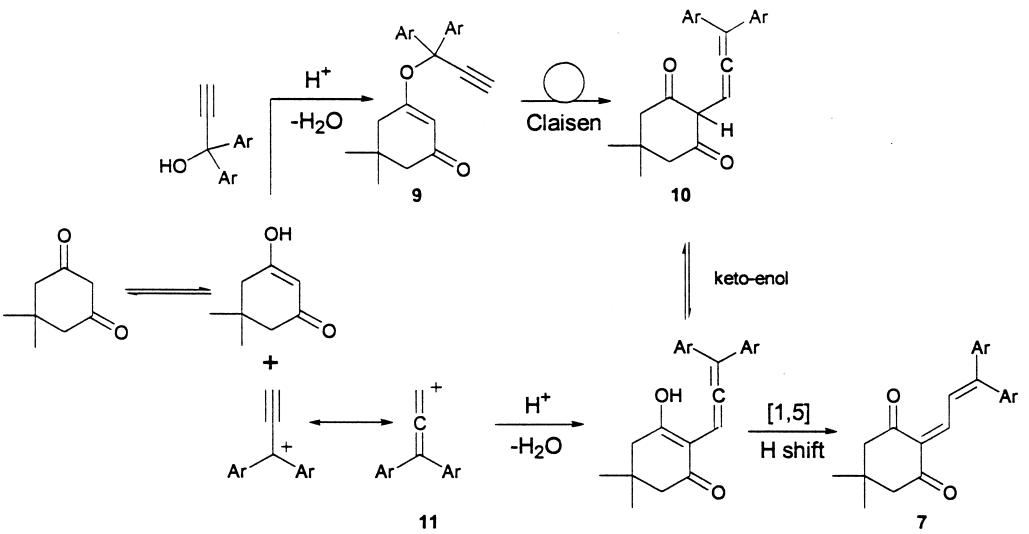
NMe_2 groups are non-equivalent and afford signals at δ 3.05 and δ 3.06. The remaining protons resonate in the expected ranges in keeping with their structural type. The presence of the carbonyl groups was confirmed by a low field signal in the ^{13}C NMR spectrum at δ 198.1 and at δ 198.7. A single C=O stretching band was observed in the infrared spectrum at 1648 cm^{-1}, a value typical for unsaturated carbonyl moieties of this type [16].

The formation of this dye may be explained by one of the two mechanisms outlined in Scheme 4. In the former, acid catalysed dehydration of **3** with interception of the cation by the enol form of dimedone gives the ether **9** which undergoes a Claisen rearrangement to generate the substituted allene **10**. Enolisation of the carbonyl group and a 1,5-hydrogen shift complete the sequence to give **7**. This mechanism is similar to that proposed for the formation of naphthopyrans from a naphthol and a propynol [1,2]. Alternatively, initial dehydration of **3** provides the resonance stabilised allenyl cation **11** in accord with a Meyer–Schuster [17] or Rupe [18] type rearrangement mechanism. The enol form of dimedone then intercepts this cation to afford the enol tautomer of **10**, which then follows the previously described pathway to give the product **7**.

Despite the fact that only the acyclic valence tautomer **7a** was isolated and that there was no evidence for the formation of the benzopyran **8a**, it was decided to investigate the synthesis and properties of some analogues of these dyes. The earlier work [6] on the merocyanine dyes **4** only considered a terminal dimethylamino group and thus the incorporation of other nitrogen donor functions was explored. Using the previous procedure, the merocyanine dyes **7b–e** were obtained in good yield (63–93%). Key ^1H NMR and UV–vis spectroscopic data for these dyes and for **7a** are presented in Table 1.

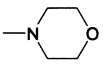
Clearly from the ^1H NMR data, the merocyanine dyes are produced in every case and they possess the same *s-trans* geometry as **7a**. Again, there was no indication of the formation of any benzopyrans **8**. Not surprisingly, the variation of the terminal donor groups on the aryl rings has negligible effect on the chemical shift and the coupling constant of the ethylene protons since no structural changes are anticipated.

However, the influence of the terminal groups is apparent from the visible spectral data. The terminal nitrogen atoms are at active sites [19] and hence any increase in the electron density at these positions should result in a red shift of the absorption band, the magnitude of which will be related to the donating ability of the terminal amino group. Examination of the λ_{max} values in Table 1 indicates



Scheme 4.

Table 1
Selected spectroscopic data for merocyanines **7**

No.	X	δ H_a	δ H_b	J_{ab} (Hz)	λ_{max} (nm)			10^{-4} ε_{max} (EtOH) (mol^{-1} dm^3 cm^{-1})
					Hexane	DMSO	EtOH	
7a	NMe_2	8.27	7.93	12.8	487	550	568	4.66
7b	NEt_2	8.26	7.98	13.0	497	570	579	5.75
7c		8.25	7.95	12.9	498	567	579	4.73
7d		8.25	7.91	12.7	479	529	548	3.14
7e		8.25	7.87	12.7	461	505	506	1.99

that in all the solvents used the pyrrolidino and diethylamino derivatives **7b** and **7c** are the most bathochromic dyes whilst the morpholino analogue **7e** not only absorbs at the shortest wavelength but is also the least intense dye.

It is well known that triphenylmethane (TPM) dyes containing diethylamino substituents absorb bathochromically of the corresponding dimethylamino derivatives. Thus, Brilliant Green absorbs ca. 8 nm and Ethyl Violet ca. 3 nm to the red of Malachite Green (MG) [20] and Crystal Violet (CV) [21], respectively. The present work corroborates these results with **7b** being 10–20 nm bathochromic of **7a**.

In the TPM system, the donating powers of diethylamino and pyrrolidino groups are found to be very similar according to spectroscopic properties [21,22]. Other approaches confirm these observations. For example, the ^{13}C NMR spectra of *N*-phenylpyrrolidine and *N,N*-diethylaniline are very similar, with the shift of the *para*-carbon indicating similar resonance interaction between the terminal nitrogen atom and the benzene ring [23]. Although ^1H NMR studies [24] and dipole moment studies of some azobenzene derivatives [25] indicate that the heterocyclic moiety conjugates more effectively than the dialkylamino function, the present work

replicates the data for the TPM series, with the greater intensity of the NEt_2 derivative in ethanol even suggesting that it is a somewhat better donor.

There is some discrepancy in the literature concerning the relative donating abilities of pyrrolidino and piperidino groups. Thus, on the basis of the changes in spectral parameters arising from increases in the acidity of the solvent system, a pyrrolidino group is better able to stabilise the positive charge associated with triphenylmethane dyes [21]. The nitrogen atom in the piperidine unit is more readily protonated than the pyrrolidine N atom indicating that it is less involved in resonance interaction with the cationic system. A similar situation is apparent in monoazo dyes containing these cyclic groups. The piperidino dyes absorb hypsochromically of the pyrrolidino analogues. Furthermore, in acidic solution, the latter dyes are protonated at the β-azo nitrogen atom whereas the piperidino compounds are protonated very largely at the terminal nitrogen atom [26]. However, λ_{max} values for the piperidino derivatives of MG, CV and Michler's Hydrol Blue (MHB) are all to the red of the corresponding pyrrolidino compounds but the intensities are significantly reduced, most notably in piperidine MHB [21]. Dreiding models indicate more interference between the equatorial hydrogen atoms of the α-methylene groups in the chair conformation of piperidine and the *ortho* protons of the adjacent phenyl ring than is apparent for the more nearly planar pyrrolidine group. Relief of strain by rotation about the terminal bonds is therefore greater for the piperidine dyes and the heteroatom is less involved in resonance. However, a study of a series of 3-aminocyclohex-2-enones has shown that the 3-pyrrolidino derivatives are more basic than the piperidino analogue [27]. In the present work the pyrrolidino derivatives absorb well to the red of the piperidino dyes.

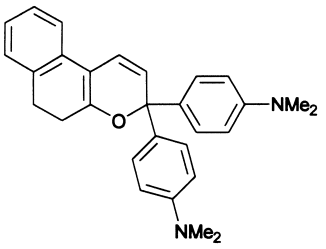
All the evidence accrued from studies on TPM and azo dyes [28] indicates that lone-pair conjugation is least efficient for the morpholino group of the five terminal groups studied as a consequence of the inductive electron withdrawal by the hetero oxygen atom. The present work supports this view since **7e** is the most hypsochromic of the five merocyanines.

The behaviour of these dyes in different solvents indicates that an increase in the polarity leads to bathochromic shifts ranging from 81–82 nm for **7a**, **7b** and **7c** to 45 nm for **7e**. The data suggest that solvent interaction changes the polarity of the dyes which are relatively weakly polar in a non-polar solvent but become significantly polar through stabilisation of the charge separated form such as **7a′** by a polar solvent.

Although both simple and fused 2*H*-pyrans coexist with the acyclic dienone with the equilibrium ratio varying with both structure and solvent, benzopyrans exist exclusively as such. Nevertheless, the O–2C bond in benzopyrans is cleaved on irradiation with UV-light, but the resulting acyclic tautomers rapidly reform the heterocyclic species when the light source is removed [8]. The dyes **7a–e** show no tendency to form the pyran **8**, a feature that can be attributed to two factors: (i) the acyclic form is stabilised by resonance and (ii) there is incomplete aromatic stabilisation of the closed species.

It was, therefore, of interest to investigate the reaction between 2-tetralone, another acidic methylene component, and propynol **3a**. Whilst the ring-closed tautomer of the product, the 5,6-dihydro-3*H*-naphtho[2,1-*b*]pyran **12**, is not a fully aromatic system, it does possess an extended conjugated pathway and is a dihydro analogue of the known photochromic compound **13** [29] and may therefore be accessible.

Using the previously described method, two coloured fractions were obtained after elution of the crude product from silica. The ^1H NMR spectrum of the less polar, major orange product indicated that this solid contained an unequal mixture of geometric isomers as shown particularly by the singlets at δ 2.98 and δ 3.04 for the non-equivalent NMe_2 groups of the minor isomer and the corresponding signals for the major isomer which appear at δ 3.00 and δ 3.03. Using the relative integrals of these pairs of signals, an approximate isomer ratio of ca. 4:3 was determined. The ethylene bridge protons of the minor isomer resonate at δ 6.95 and at δ 7.64 with a coupling constant of 12.2 Hz indicating an *s-trans* arrangement. For the major isomer, although only one of the signals is visible, δ 8.21, a coupling constant of 12.0 Hz



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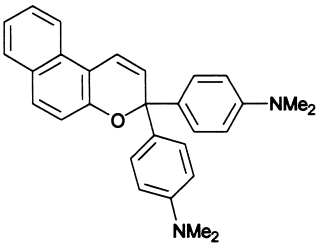

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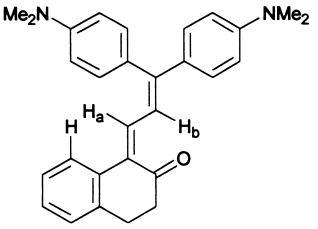

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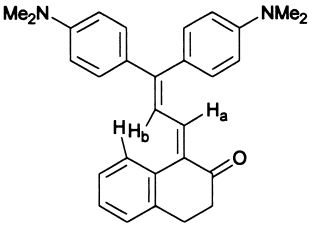

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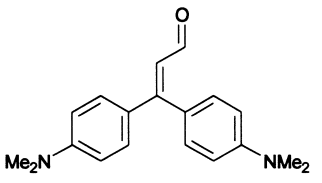
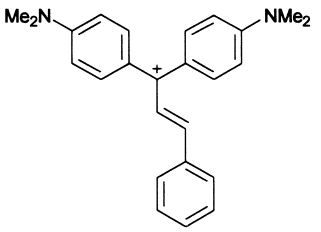


16

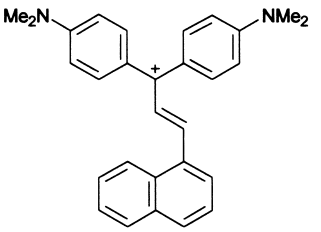
again confirms an *s-trans* arrangement. From this NMR data, it is clear that the product is a mixture of two isomeric merocyanines **14** and **15** and does not contain any naphthopyran **12**. The maximum absorption band for this mixture of isomers is shifted hypsochromically relative to dyes **7**, with λ_{max} (EtOH) 466 nm ($\varepsilon_{max} = 2.83 \times 10^4$ mol^{-1} dm^3 cm^{-1}), as a consequence of only a single C=O acceptor group in the molecule.

The structures **14** and **15** bear a close resemblance to the TPM dye system such as Malachite Green (MG) in which steric congestion arising at the *ortho*-positions prevents planarity and the basic structure is that of a three-bladed propeller with the rings twisted ca. 30° out of the sp^2 plane defined by the central carbon atom and its three bonds [30]. Closer structural relationships are apparent with the vinylogue of MG **17a** and the vinylogue of the Victoria Blue dye **17b**. In both of these dyes, the vinyl group does not appear to relieve steric crowding since, although both absorption bands show red shifts, there is a collapse in the intensity of the major band [31]. In the case of **17b**, this feature suggests that the naphthyl unit may cause further congestion along the dimethylaminophenyl-C-dimethylaminophenyl axis.

Space filling molecular models confirm similar congestion for the isomers **14** and **15** about the ethylene bridge with significant deviations from planarity apparent for both isomers. Particularly noticeable are clashes between H-8 and the ethylene protons and between the *ortho* hydrogen atoms of



17a



17b

the dimethylaminophenyl rings and the ethylene protons. In such complex crowded molecules, the assignment of structures to the major and minor isomers cannot be made with any certainty, even after the information obtained from the space filling models has been considered. However, the close similarity between the chemical shift of the low field signal at δ 8.21 associated with the major isomer in the ^{1}H NMR spectrum and that of H_a (ca. δ 8.25) in the merocyanines **7** would suggest that a similar structural arrangement is present. From this it follows that **15** is the structure of the major isomer.

The second, more polar yellow component isolated from this reaction was characterised as the α,β-unsaturated aldehyde **16**. The ^{1}H-NMR spectrum of this compound displayed a low field doublet at δ 9.46 with *J* 8.0 Hz coupled to the signal at δ 6.41. These signals are assigned to the aldehyde and alkenyl protons of **16**, respectively. The infrared spectrum of **16** displayed a C=O stretching band at 1649 cm^{-1}, a value that is typical for an α,β-unsaturated C=O group. The structure of this compound was confirmed by the close correlation of its melting point with that of authentic material [32]. The formation of this material merits some comment. Initial dehydration of the propynol **3a** affords the resonance stabilised allenic cation **11** as previously discussed (Scheme 4). Interception of the cation **11** by water and subsequent enol–keto tautomerism results in **16**. The formation of the 3,3-diarylprop-2-enal **16** by this route provides a useful alternative to the classic approaches to these compounds that utilise either Vilsmeier–Haack [32] or Wadsworth–Emmons [33] type chemistry. Such compounds are valuable intermediates for the synthesis of photochromic naphthopyrans by the titanium(IV) ethoxide protocol [34].

Dehydrogenation of a mixture of the isomers **14** and **15** was accomplished using *p*-chloranil in refluxing toluene and resulted in the spontaneous cyclisation to the naphthopyran **13**, which was obtained in 36% yield after column chromatography. It therefore seems clear that a completely aromatic system is a prerequisite for ring closure of the merocyanines. The naphthopyran **13** is photochromic and its physical and spectroscopic properties are in full accord with those reported previously [29]. This dehydrogenation protocol constitutes a new route to this class of photochromic naphthopyran.

3. Experimental

Flash chromatography was performed using silica grade C-560 as supplied by Fluorochem Ltd. according to the published procedure [35]. Melting points were recorded in capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer in KBr discs unless otherwise specified. NMR spectra were recorded in $CDCl_3$ using a Jeol lambda series 400 MHz instrument; coupling constants are quoted in Hz. Visible spectra were recorded in either spectroscopic grade ethanol or dimethyl sulfoxide in 1 cm quartz cells using a Perkin Elmer λ5 spectrophotometer.

3.1. Preparation of 1,1-bis(4-aminoaryl)prop-2-yn-1-ols

n-Butyllithium (2.5 M in hexanes) (30 mmol) was added slowly via syringe to a cold (−10°C), stirred solution of trimethylsilylacetylene (30 mmol) in anhydrous tetrahydrofuran (100 cm^3) under a nitrogen atmosphere. On completion of the addition (ca. 5 min), the cold solution was stirred for 1 h. A slurry of the benzophenone (30 mmol) in anhydrous tetrahydrofuran (50 cm^3) was then added in a single portion and the mixture was stirred until TLC examination of the reaction mixture indicated that no benzophenone remained (ca. 3 h). The solution was then diluted with water (50 cm^3) and aqueous saturated ammonium chloride solution (50 cm^3). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (2×50 cm^3). The combined organic extracts were washed with water (50 cm^3), dried (Na_2SO_4) and evaporated to give the crude 3-trimethylsilylprop-2-yn-1-ol. Tetra-*n*-butylammonium fluoride (1 M tetrahydrofuran) (36 mmol) was added to a cold (0°C) stirred solution of the crude silylpropynol in tetrahydrofuran (75 cm^3). The solution was stirred until TLC examination indicated that no silylpropynol remained (ca. 15 min). The mixture

was poured into water (200 cm^3) and extracted with ethyl acetate (4×75 cm^3). The combined organic extracts were washed with water (5×50 cm^3), dried (Na_2SO_4) and evaporated to give the alkynol which was sufficiently pure for subsequent use. The following propynols were obtained in this way.

3.1.1. 1,1-Bis(4-N,N-dimethylaminophenyl)prop-2-yn-1-ol **3a**

From 4,4′-bis(*N*,*N*-dimethylamino)benzophenone as an off-white powder (86%) after recrystallisation from ethyl acetate and hexane, m.p. 158.0–160.0°C (lit. m.p. 154–155°C [36]); υ_{max} (Nujol) 3351, 3252, 2110, 1611 cm^{-1}; δ_H 2.75 (1H, s, alkynic-H), 2.97 (1H, bs, OH), 3.23 (12H, s, $(NMe_2)_2$), 6.88 (4H, m, Ar-H), 7.64 (4H, m, Ar-H).

3.1.2. 1,1-Bis(4-N,N-diethylaminophenyl)prop-2-yn-1-ol **3b**

From 4,4′-bis(*N*,*N*-diethylamino)benzophenone as a pale green powder (84%) after recrystallisation from ethyl acetate and hexane, m.p. 146.0–147.0°C; υ_{max} (Nujol) 3339, 3250, 2115, 1605, 1509 cm^{-1}; δ_H 1.19 (12H, t, *J* 7, $(CH_3)_4$), 2.61 (1H, s, alkynic-H), 2.84 (1H, bs, OH), 3.38 (8H, q, *J* 7, $(N(CH_2)_2)_2$), 6.57 (4H, m, Ar-H), 7.45 (4H, m, Ar-H). (Found: C, 78.8; H, 8.6; N, 8.1. $C_{23}H_{30}N_2O$ requires C, 78.8; H, 8.6; N, 8.0%.)

3.1.3. 1,1-Di(4-pyrrolidinophenyl)prop-2-yn-1-ol **3c**

From 4,4′-dipyrrolidinobenzophenone as a pale orange powder (79%) after recrystallisation from ethyl acetate and hexane, m.p. 162.5–164.5°C; υ_{max} (Nujol) 3346, 3236, 2117, 1606, 1510 cm^{-1}; δ_H 1.83 (8H, m, $(CH_2)_4$), 2.37 (1H, bs, OH), 2.62 (1H, s, alkynic-H), 3.09 (8H, m, $(N(CH_2)_2)_2$), 6.32 (4H, m, Ar-H), 7.23 (4H, m, Ar-H). (Found: C, 79.8; H, 7.8; N, 8.2. $C_{23}H_{26}N_2O$ requires C, 79.7; H, 7.6; N, 8.1%.)

3.1.4. 1,1-Di(4-piperidinophenyl)prop-2-yn-1-ol **3d**

From 4,4′-dipiperidinobenzophenone as an off-white powder (83%) after recrystallisation from ethyl acetate and hexane, m.p. 151.5–153.0°C; υ_{max} (Nujol) 3395, 3231, 2119, 1612, 1511 cm^{-1}; δ_H 1.70 (12H, m, $(CH_2)_6$), 2.82 (1H, bs, OH), 2.85 (1H, s, alkynic-H), 3.19 (8H, m, $(N(CH_2)_2)_2$), 6.90 (4H, m, Ar-H), 7.45 (4H, m, Ar-H). (Found: C, 80.3; H, 8.2; N, 7.8. $C_{25}H_{30}N_2O$ requires C, 80.2; H, 8.1; N, 7.5%.)

3.1.5. 1,1-Di(4-morpholinophenyl)prop-2-yn-1-ol **3e**

From 4,4′-dimorpholinobenzophenone as an off-white powder (96%) after recrystallisation from ethyl acetate and hexane, m.p. 226.0–228.0°C; υ_{max} (Nujol) 3418, 3227, 2120, 1608, 1512 cm^{-1}; δ_H 2.81 (1H, bs, OH), 2.88 (1H, s, alkynic-H), 3.18 (8H, m, $(N(CH_2)_2)_2$), 3.88 (8H, m, $(O(CH_2)_2)_2$), 6.89 (4H, m, Ar-H), 7.51 (4H, m, Ar-H). (Found: C, 73.1; H, 7.0; N, 7.5. $C_{23}H_{26}N_2O_3$ requires C, 73.0; H, 6.9; N, 7.4%.)

3.2. General method for the preparation of the merocyanine dyes **7**

4-Toluenesulfonic acid monohydrate (0.05g) was added to a stirred solution of dimedone (6.9 mmol) and a propynol **3** (6.9 mmol) in anhydrous toluene (75 cm^3) and the mixture was refluxed until TLC examination of the reaction mixture indicated that no propynol remained (ca. 30 min). Removal of the toluene gave an intense red gum that solidified on addition of hexane and ethyl acetate with scratching. The crude merocyanine was collected by vacuum filtration and recrystallised. The following compounds were obtained by this protocol.

3.2.1. 5,5-Dimethyl-2[3,3-bis(4-dimethylaminophenyl)propylidene]cyclohexane-1,3-dione **7a**

As deep red/purple crystals from ethyl acetate and hexane (85%), m.p. 209–211°C; υ_{max} 1648, 1603, 1504 cm^{-1}; δ_H 1.08 (6H, s, 5-Me_2), 2.46 (2H, s, CH_2), 2.51 (2H, s, CH_2), 3.05 (6H, s, NMe_2), 3.06 (6H, s, NMe_2), 6.64 (2H, m, Ar-H), 6.72 (2H, m, Ar-H), 7.17 (2H, m, Ar-H), 7.40 (2H, m, Ar-H), 7.93 (1H, d, *J* 12.8, H_b), 8.27 (1H, d, *J* 12.8, H_a); δ_C 28.6, 30.3, 40.1, 52.4, 54.0, 111.3, 120.7, 125.0, 126.0, 129.0, 132.4, 133.7, 151.8, 152.0, 152.1, 168.2, 198.1, 198.7. (Found C, 77.9; H, 7.9; N, 6.9. $C_{27}H_{32}N_2O_2$ requires C, 77.8; H, 7.8; N, 6.7%.)

3.2.2. 2[3,3-bis(4-Diethylaminophenyl)propylidene]-5,5-dimethyl-cyclohexane-1,3-dione **7b**

As deep red/purple crystals from ethyl acetate and hexane (69%), m.p. 169–171°C; υ_{max} 1640, 1598, 1497 cm^{-1}; δ_H 1.08 (6H, s, 5-Me_2), 1.22

(12H, m, $(CH_3)_4$), 2.45 (2H, s, CH_2), 2.50 (2H, s, CH_2), 3.42 (8H, m, $(N(CH_2)_2)_2$), 6.60 (2H, m, Ar-H), 6.67 (2H, m, Ar-H), 7.16 (2H, m, Ar-H), 7.41 (2H, m, Ar-H), 7.98 (1H, d, *J* 13.0, H_b), 8.26 (1H, d, *J* 13.0, H_a). (Found C, 78.8; H, 8.8; N, 6.1. $C_{31}H_{40}N_2O_2$ requires C, 78.8; H, 8.5; N, 5.9%.)

3.2.3. 5,5-Dimethyl-2[3,3-bis(4-pyrrolidinophenyl)propylidene]cyclohexane-1,3-dione **7c**

As deep red/purple crystals from ethyl acetate and hexane (78%), m.p. 184–186°C; υ_{max} 1638, 1602, 1507 cm^{-1}; δ_H 1.08 (6H, s, 5-Me_2), 2.04 (8H, m, $(CH_2)_4$), 2.45 (2H, s, CH_2), 2.50 (2H, s, CH_2), 3.36 (8H, m, $(N(CH_2)_2)_2$), 6.50 (2H, m, Ar-H), 6.58 (2H, m, Ar-H), 7.17 (2H, m, Ar-H), 7.41 (2H, m, Ar-H), 7.95 (1H, d, *J* 12.9, H_b), 8.25 (1H, d, *J* 12.9, H_a). (Found C, 79.6; H, 7.8; N, 6.1. $C_{31}H_{36}N_2O_2$ requires C, 79.4; H, 7.7; N, 6.0%.)

3.2.4. 5,5-Dimethyl-2[3,3-bis(4-piperidinophenyl)propylidene]cyclohexane-1,3-dione **7d**

As deep red/purple crystals from ethyl acetate and hexane (63%), m.p. 180–183°C; υ_{max} 1637, 1601, 1517 cm^{-1}; δ_H 1.08 (6H, s, 5-Me_2), 1.67 (12H, m, $(CH_2)_6$), 2.46 (2H, s, CH_2), 2.51 (2H, s, CH_2), 3.31 (8H, m, $(N(CH_2)_2)_2$), 6.81 (2H, m, Ar-H), 6.92 (2H, m, Ar-H), 7.13 (2H, m, Ar-H), 7.36 (2H, s, Ar-H), 7.91 (1H, d, *J* 12.7, H_b), 8.25 (1H, d, *J* 12.7, H_a). (Found C, 80.0; H, 8.2; N, 5.7. $C_{33}H_{40}N_2O_2$ requires C, 79.8; H, 8.1; N, 5.6%.)

3.2.5. 5,5-Dimethyl-2[3,3-bis(4-morpholinophenyl)propylidene]cyclohexane-1,3-dione **7e**

As deep red crystals from ethyl acetate and hexane (93%), m.p. 207–209°C; υ_{max} 1641, 1603, 1516 cm^{-1}; δ_H 1.08 (6H, s, 5-Me), 2.47 (2H, s, CH_2), 2.53 (2H, s, CH_2), 3.16 (8H, m, $(N(CH_2)_2)_2$), 3.87 (8H, m, $(O(CH_2)_2)_2$), 6.89 (2H, m, Ar-H), 7.15 (2H, m, Ar-H), 7.38 (2H, m, Ar-H), 7.47 (2H, m, Ar-H), 7.87 (1H, d, *J* 12.7, H_b), 8.25 (1H, d, *J* 12.7, H_a). (Found C, 74.4; H, 7.4; N, 5.8. $C_{31}H_{36}N_2O_4$ requires C, 74.4; H, 7.3; N, 5.6%.)

3.2.6. 1[3,3-Bis(4-dimethylaminophenyl)propylidene]-1,2,3,4-tetrahydronaphthalen-2-one **14**, **15**

Elution of the crude reaction product from silica with 10% EtOAc in toluene gave two fractions. Fraction 1, the title isomers **14**, **15** as orange plates from ethyl acetate and hexane (46%), m.p. 205–208°C; υ_{max} 1674, 1604, 1547, 1523, 1359 cm^{-1}, λ_{max} (EtOH) 466 nm, ε_{max} 28290 mol^{-1} dm^3 cm^{-1}; δ_H (major) 2.66 (2H, t, *J* 6.1, 4-H), 2.96 (2H, t, *J* 6.1, 3-H), 3.00 (6H, s, NMe_2), 3.03 (6H, s, NMe_2), 6.64 (2H, m, Ar-H), 6.75 (2H, m, Ar-H), 7.20 (9H, m, Ar-H, alkenic-H), 8.21 (1H, d, *J* 12.0, alkenic-H). In addition, the following distinct signals were observed for the minor isomer δ_H (minor) 2.57 (2H, t, *J* 6.1, 4-H), 2.98 (6H, s, NMe_2), 3.04 (6H, s, NMe_2), 6.95 (1H, d, *J* 12.2, alkenic-H), 7.33 (2H, m, Ar-H), 7.64 (1H, d, *J* 12.2, alkenic-H), 7.65 (1H, m, Ar-H). (Found for mixture MH^+, 423.2438; C, 82.5; H, 7.3; N, 6.8. $C_{29}H_{30}N_2O$ requires MH^+, 423.2436(4); C, 82.4; H, 7.2; N, 6.6%.) Fraction 2, 3,3-bis(4-dimethyl-aminophenyl)prop-2-enal **16** as yellow-green plates from ethyl acetate and hexane (21%), m.p. 170–172°C (lit. m.p. 171–172°C [32]); υ_{max} 2895, 2747, 1649, 1607 cm^{-1}; δ_H 3.02 (6H, s, NMe_2), 3.04 (6H, s, NMe_2), 6.41 (1H, d, *J* 8.0, 2-H), 6.50 (2H, m, Ar-H), 6.72 (2H, m, Ar-H), 7.20 (2H, m, Ar-H), 7.30 (2H, m, Ar-H), 9.46 (1H, d, *J* 8.0, 1-H).

3.3. Preparation of 3,3-bis(4-N,N-dimethylaminophenyl)-3H-naphtho[2,1-b]pyran **13**

A solution of the 1[3,3-bis(4-dimethylaminophenyl)propylidene]-1,2,3,4-tetra hydronaphthalen-2-ones **14**, **15** (2.36 mmol) and *p*-chloranil (2.6 mmol) in toluene (40 cm^3) was boiled under reflux for 20 h and then cooled to room temperature. Removal of the toluene gave a black solid which was eluted from silica with 30% EtOAc in hexane to afford the title compound **13** as off-white microcrystals after recrystallisation from hexane and EtOAc, (36%), m.p. 221.0–222.0°C (lit. m.p. 223°C [29]); λ_{max} (PhMe) 558, 446 nm; δ_H 2.96 (12H, s, $(NMe_2)_2$), 6.26 (1H, d, *J* 10.0, 2-H), 6.75 (4H, m, Ar-H), 7.21 (1H, d, *J* 8.8, 5-H), 7.38 (7H, m, Ar-H, 1-H), 7.67 (1H, d, *J* 8.8, 6-H), 7.74 (1H, m, Ar-H), 7.99 (1H, m, Ar-H). (Found: M^+, 420.2209; C, 82.8; H, 6.7; N, 6.8. $C_{29}H_{28}N_2O$ requires M^+, 420.2201(6); C, 82.7; H, 6.7; N, 6.7%.)

4. Conclusions

The reaction of dimedone with aminoarylpropynols affords intensely coloured merocyanines

rather than tetrahydrobenzopyrans, their ring-closed valence tautomers. However, aromatisation of the product from 2-tetralone and the dimethylaminophenylpropynol allows cyclisation to the photochromic naphthopyran.

Acknowledgements

We thank the EPSRC and James Robinson Ltd (Huddersfield) for an Industrial CASE award to D.A.T. and the EPSRC for the provision of a HRMS service at the University of Wales, Swansea.

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