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Structural elucidation of the red dye obtained from reaction of 1,8-naphthalenediol with 1,1-diphenylprop-2-yn-1-ol. A correction

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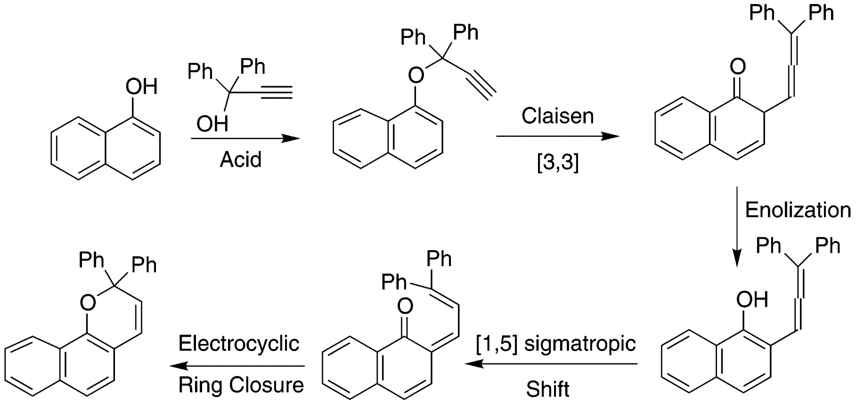
Abstract—The structure of the intensely coloured red product obtained through the reaction of 1,8-naphthalenediol with 1,1-diphenylprop-2-yn-1-ol was reinvestigated. Instead of the expected permanent open form of the naphthopyran, the dye presents the α,β-unsaturated chain at a different position of the naphthalene nucleus. The structure of this compound was elucidated on the basis of detailed spectral analysis, including 2D NMR experiments. © 2003 Elsevier Science Ltd. All rights reserved.

The reaction of naphthols with 1,1-diarylprop-2-yn-1-ols under acid catalysis gives naphthopyrans in medium yield. The accepted mechanism involves the in situ formation of an aryl propynyl ether which undergoes a Claisen rearrangement followed by enolisation, sigmatropic [1,7] H-shift and finally an electrocyclic ring closure (Scheme 1).[1]

There is considerable interest in these compounds as they exhibit a photochromic behaviour at room temperature, in solution or in polymeric matrices.[2] Under near-UV irradiation, a reversible ring opening reaction takes place, leading to a highly conjugated coloured form (Scheme 2).

In a recent study, we reported that the reaction of 1,8-naphthalenediol with 1,1-diphenylprop-2-yn-1-ol under pyridinium *p*-toluenesulphonate (PPTS) catalysis gave a highly coloured red dye in 65% yield.[3] No naphthopyrans were found in the reaction mixture. Spectroscopic analysis (^{1}H and ^{13}C NMR, IV, UV, HRMS) of the product was consistent with structure **B**,



Scheme 1.

Keywords: naphthopyrans; 1,8-naphthalenediol; dye; hydrogen-bond.

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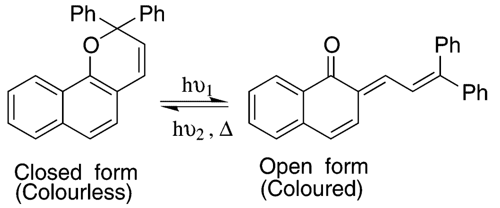


Scheme 2.

indicating that the product could be a naphthopyran open form, stabilised through an intramolecular H-bond (Scheme 3).[3]

A more detailed structural study was achieved by further long range correlations observed in bi-dimensional NMR studies and revealed that the correct structure for the product is in fact the *para*-isomer **A**. To decide whether structure **A** or structure **B** corresponds to the product is not a straightforward task because almost all the NMR spectral data (Table 1) can be assigned considering both structures.

The key-feature was found in the HMBC spectrum where a cross peak between the signal δ_H 7.10 (H-5) and a quaternary carbon signal at δ_C 128.5 (C-4) requires that the α,β-unsaturated chain must be located at this carbon (Fig. 1). Further information that supported the position of the α,β-unsaturated chain was obtained from NOE experiments which are also listed in Table 1. The observed effects between the signals δ_H 7.10 (H-5) and δ_H 7.68 (H-1′) confirms the spatial proximity of these protons as depicted in Fig. 1, excluding the possibility of structure **B**.

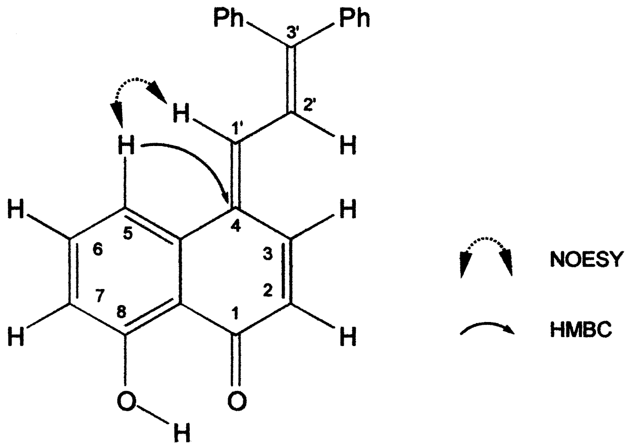
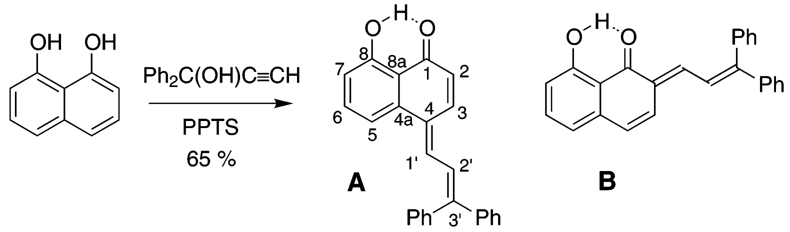


Figure 1. Revealing C/H and H/H long-range correlations obtained from the HMBC and NOESY spectra.

Recently, Heron et al. reported that the reaction of 1-naphthol with 1,1-diphenylprop-2-yn-1-ol under



Scheme 3.

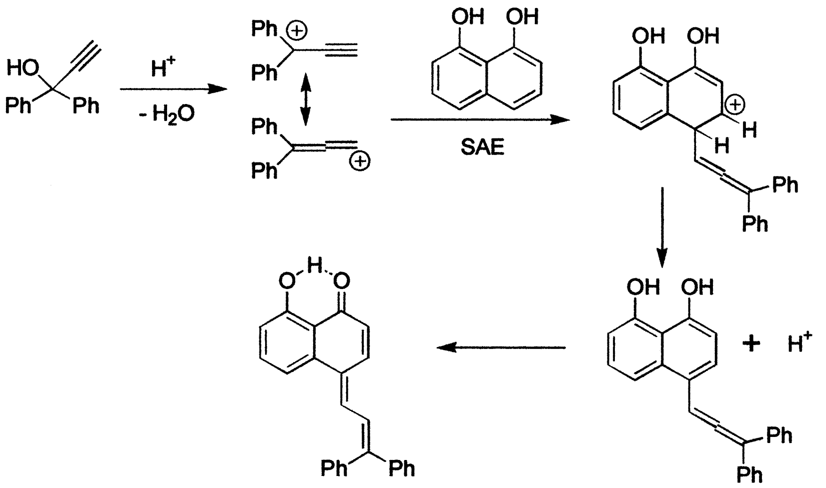
Table 1. NMR spectral data of the red dye **A**

Atom	^{1}H (J in Hz)	^{13}C	^{1}H–^{1}H COSY	HMBC	NOESY
1	–	190.0	–	–	–
2	6.56, *dd* (10.0, 1.4[b])	126.3	H-3, H-1′	C-4, C-8a	H-3
3	8.09, *br d* (10.0)	137.1	H-2	C-1, C-4, C-4a, C1′	H-2, H-2′
4	–	128.5[a]	–	–	–
4a	–	136.9	–	–	–
5	7.10, *br d* (8.0)	112.8	H-6	C-4, C-6, C-7, C-8a	H-6, H-1′
6	7.38, *dd* (8.0)	134.1	H-5, H-7	C-4a, C-5, C-8, C-8a	H-5, H-7
7	6.93, *br d* (8.1)	116.2	H-6	C-5, C-8, C-8a	H-6
8	–	162.5	–	–	–
8a	–	115.9	–	–	–
1′	7.68, *br d* (12.2)	136.6	H-2, H-2′	C-3, C-4a, C-3′	H-5, H-2′
2′	7.53, *br d* (12.2)	122.3	H-1′	C-4	H-3, H-1′
3′	–	153.3	–	–	–
-O$\underline{H}$	13.29, *s*	–	–	C-7, C-8, C-8a	–

All ^{1}H–^{13}C connectivities were assigned by HSQC experiments. NOE difference experiments confirmed the following spatial correlations: H-2 with H-3; H-3 with H-2 and H-2′.

[a] Approximate value due to overlapped signals.

[b] Long range coupling (^5J).



Scheme 4.

APTS catalysis gives, in addition to the expected naphthopyran, 1% of a coloured dye with the conjugated system at C-4 of the naphthalene nucleus. When starting from 2-methyl-1-naphthol, which cannot give the naphthopyran product, the yield was improved to 19%.[4] The authors suggested a mechanism involving the electrophilic aromatic substitution of the naphthol by the allenyl cation derived from a Meyer–Schuster rearrangement of the 1,1-diarylprop-2-yn-1-ol.[5]

The absence of the usual naphthopyran product in the reaction of 1,8-naphthalenediol with 1,1-diphenylprop-2-yn-1-ol can be explained by the intramolecular H-bond between the two hydroxylic substituents which may prevent the formation of the intermediate arylpropynyl ether that leads to the naphthopyran. It is possible that the red dye **A** is formed through the mechanism proposed by Heron (Scheme 4), but it is not clear why the product from the *para* attack of the allenyl cation to the naphthalene nucleus is the only one observed.

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