Naphthoquinone Methide Type Near-I.R. Dye: The Properties and Structure of 4-(2'-Acetylamino-4'-diethylaminophenylimino)-1,4-dihydronaphthylidenemalononitrile

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The introduction of an acetylamino group at the 2'-position in the aniline ring of a naphthoquinone methide dye produced a red shift with a large increase in the molecular extinction coefficient in $CHCl_3$ solution, and an intramolecular ring-closure reaction of the compound under alkaline conditions gave a new blue dye; the stereochemistry of this chromophoric system was determined by *X*-ray analysis.

In recent years, near-i.r. dyes have attracted considerable attention as suitable dyes for use in the field of diode-laser optical storage.[1] These dyes must adequately absorb the near-i.r. light emitted from a diode-laser. We have already proposed that the new deep coloured naphthoquinone methide dyes absorb near-i.r. light at 722—761 nm ($\varepsilon_{max.}$ 24 200—30 800 l mol^{-1} cm^{-1}) in $CHCl_3$ solution and have good film properties for use as diode-laser optical storage media.[2] Therefore, it is important to synthesize related derivatives and clarify the stereochemistry of this dye in order to evaluate the colour–structure relationship.

In this paper, we report the properties of the title compound produced by the introduction of an acetylamino group into the 2'-position of the naphthoquinone methide dye, and the stereochemistry of this chromophoric system is discussed on the basis of the results of *X*-ray analysis.

The naphthquinone methide derivative (**3**)† was synthesized in 56% yield by condensing 1-naphthylmalononitrile (**1**)[3] with 2-acetylamino-4-diethylaminoaniline (**2**) in alkaline solution, at room temperature, in the presence of ammonium peroxydisulphate (Scheme 1). The dye (**3**) absorbs near-i.r. light at 772 nm ($\varepsilon_{max.}$ 59 000 l mol^{-1} cm^{-1}) in $CHCl_3$ solution. As shown in Table 1, the introduction of acetylamino group produced a 34 nm red shift and, in particular, the molecular extinction coefficient was almost twice that of (**4**).[2] These absorption properties were caused by the electronic properties and steric effect of the acetylamino group at the 2'-position in the aniline ring. Especially, the large increase in the molecular extinction coefficient suggested that the torsion between the quinone imine (acceptor) and the aniline (donor) moiety decreased. Conjugation between the two moieties is strengthened by the intramolecular hydrogen bonding between the peptide segment of acetylamino group and the imino nitrogen. Further, the intramolecular hydrogen bonding might enhance the strength of the electron accepting property of the imino segment.

The intramolecular ring-closure reaction of (**3**) in KOH/

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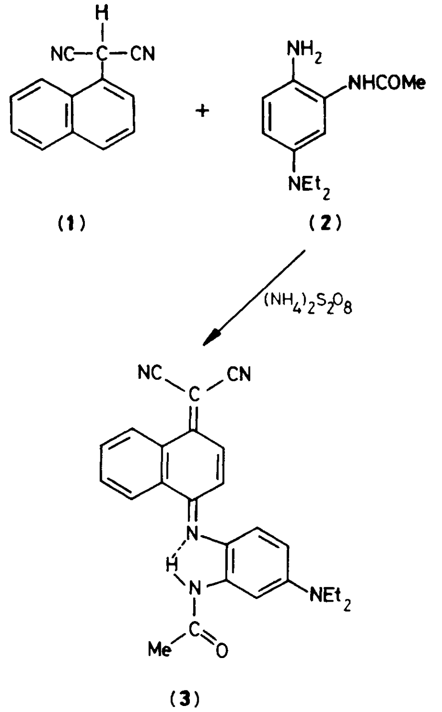
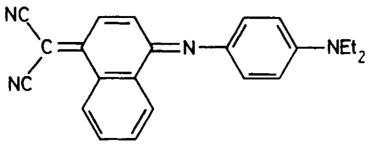
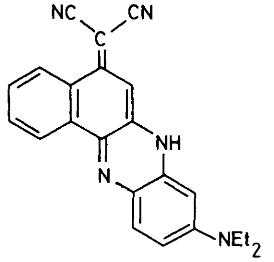
† The structure assignments were based on observed analytical data.



Scheme 1



(4)



(5)

EtOH solution at room temperature gave the benzophenazine (5)[†] in 75% yield. The dye (5) is blue in colour and has an intense absorption band at 651 nm ($\varepsilon_{max.}$ 50 700 l mol^{-1} cm^{-1}) in $CHCl_3$ solution, whose wavelength is shorter than that of (3) by 121 nm. Since the bridging nitrogen atom acts as donor to both moieties, the absorption band is largely shifted compared to the open chain structure. This large hypsochromic shift by ring-closure from the near-i.r. to the visible wavelength region should have applications in the design of new functional dyes.

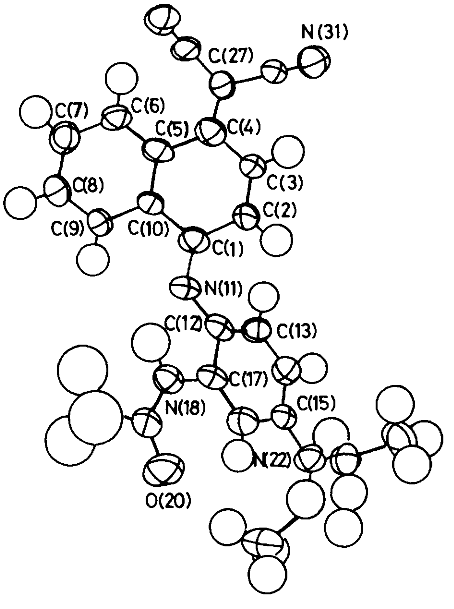


Figure 1. Molecular structure of dye (3). *Selected interatomic distances*: C(1)–C(2), 1.424(5); C(2)–C(3), 1.352(5); C(3)–C(4), 1.433(5); C(1)–N(11), 1.321(4) Å. *Selected angle*: C(1)–N(11)–C(12), 124.9(3)°.

Table 1. Light absorption properties of dyes (3), (4), and (5).

Dye	$\lambda_{max.}$/nm ($CHCl_3$)	$\varepsilon_{max.}$/l mol^{-1} cm^{-1} ($CHCl_3$)
(3)	772	59 000
(4)	738	30 800
(5)	651	50 700

The structure of dye (3) has been determined by *X*-ray analysis[‡] as shown in Figure 1. As expected, the intramolecular overcrowding disturbs the coplanarity of this molecule. In the quinone imine moiety, four atoms [N(11)=C(1)–C(2)=C(3)] lie in a plane (plane I). The ring formed by C(5)—C(10) is almost planar and is tilted from plane I by 8.59(5)°. The C(4) atom deviates significantly from these planes; the plane through C(3), C(4), and C(5) is tilted from the plane through C(2), C(3), C(5), and C(10) by 9.8(4)°. An intramolecular hydrogen bond is formed between the imino nitrogen and peptide segment in the acetylamino group. The interatomic distances of N(11)–N(18) and N(11)–H are 2.636(1) and 2.179(1) Å, respectively and the angle

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[‡] *Crystal data* for (3): $C_{25}H_{23}N_5O$, M = 409.5, orthorhombic, space group $P2_12_12_1$, a = 16.806(2), b = 16.880(4), c = 7.421(3) Å, U = 2105(2) Å^3, Z = 4, D_c = 1.29 g cm^{-3}, μ(Cu-K_α) = 5.71 cm^{-1}, $F(000)$ = 864. The lattice constants were determined by a CAD-4 indexing program and refined by a least-squares method with the angular settings of 12 reflections ($2\theta > 50°$). Data were collected on an Enraf-Nonius CAD-4 diffractometer with Cu-K_α radiation (λ = 1.5418 Å) monochromatized by a graphite crystal. 2508 Reflections were measured in the range $2\theta < 149°$, of which 2239 with $|F_o| > \sigma(|F_o|)$ were considered as observed and used for the structure determination. Lorentz and polarization corrections were applied. The structure was solved by the direct method[5] and refined by full-matrix least-squares.[6] The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma(F)^2 + 0.046637F^2]$. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms could be located on a difference Fourier map, but their positions were recalculated geometrically and included in the refinement procedure with isotropic thermal parameters. The final R value was 0.067, R_w = 0.085, $(\Delta/\sigma)_{max.}$ = 0.336. There was no peak greater than 0.3 eÅ^{-3} on the final difference Fourier map. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

N(11)–H–N(18) is 106.0(0)°. The interference between the hydrogens attached to C(2) and C(13) seems to be the reason why the aniline ring is tilted out of plane I by 42.60(3)°. However, the interatomic distance between them is 2.119 Å, which is shorter than the sum of the van der Waals radii (2.34 Å),[4] may be caused by a balance between steric and electronic factors. It is notable that the dye (**3**) which has this steric torsion absorbs near-i.r. light. Therefore, theoretical treatment by M.O. calculations is under investigation.

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