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2-METHYLBENZ[*c*,*d*]INDOLE AND ITS DERIVATIVES

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SUMMARY

2-Methylbenz[c,d]*indole was prepared from naphthostyril 2-Methyl- and 2-methylthio-benz*[c,d]*indoles gave 2-[(benz*[c,d]*indole-2*(1H)*-ylidene)methyl]benz*[c,d]*-indole in good yield Visible spectra of methine dyes originating from this base were considered*

1 INTRODUCTION

Among all nitrogen heterocycles benz[*c*,*d*]indole forms the most deeply coloured dyes with equal lengths of polymethine chain [1] As the stability of methine dyes becomes less as the polymethine chain is extended, so the benz[*c*,*d*]indole nucleus gives rise to stable infrared dyes Thus dyes containing this nucleus may be used as Q-switches for lasers on Nd^{3+} with emission wavelength 1·06 mkm [2]

Up to the present time the 2-methylbenz[*c*,*d*]indole quaternary salts have been synthesised directly from the *N*-alkylnaphthostyrils,[1, 3] omitting the preparation of the base. An alternative route has recently been proposed There have been several unsuccessful attempts to find an alternative route [4-7] A recent paper[8] has claimed the synthesis of 2-alkyl(aryl)benz[*c*,*d*]indoles, and in particular the 2-methyl derivative, by heating acyl-α-naphthylamines with phosphorus oxychloride in nitrobenzene. The formation of benz[*c*,*d*]indoles was supported by i r. spectra and molecular weight determinations Regrettably the authors did not mention details of the synthesis and the yields of products

We failed to isolate individual products on attempting to repeat this synthesis using acetyl-α-naphthylamine. Consequently, 2-methylbenz[*c*,*d*]indole was obtained from 2-methylthiobenz[*c*,*d*]indolium iodide (1). This salt is readily prepared from naphthostyril.[9]

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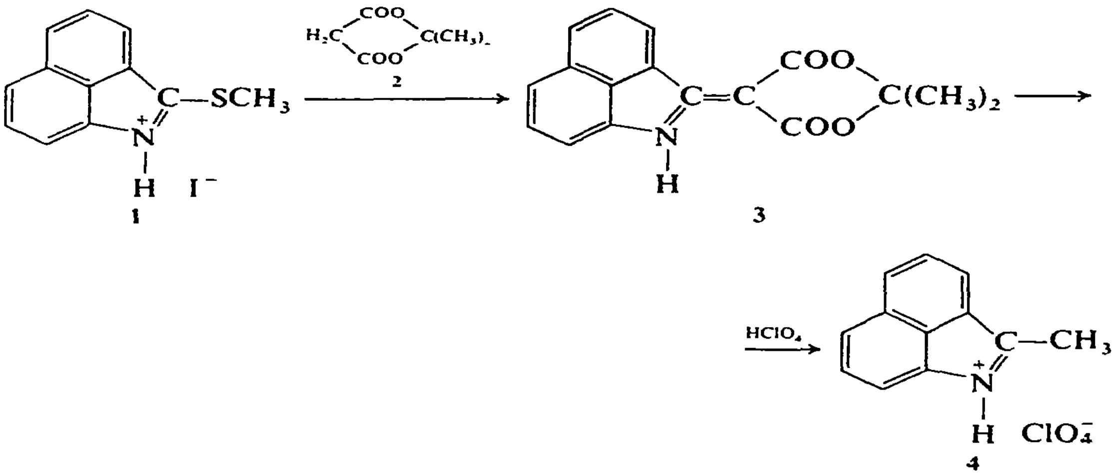
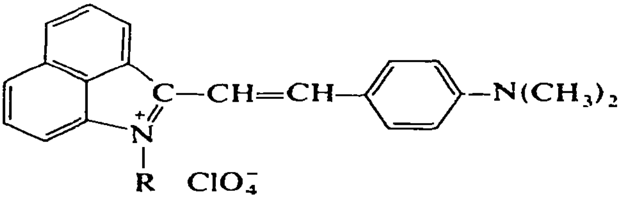


The protons of the methyl group in the perchlorate 4 (CF_3COOH) give rise to a singlet at 3 1 ppm in the p m r spectrum With *p*-dimethylaminobenzaldehyde this salt gives the dye 5 (R = H)



R = H, CH_3

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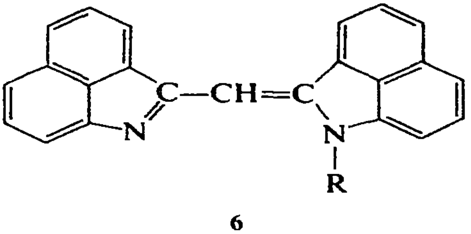
Treatment with a base and subsequent alkylation with dimethylsulphate converts this dye into 5 ($R = CH_3$) The same dye may also be obtained from 2-methylbenz[*c*,*d*]indole quaternary salt We were not able to isolate 2-methylbenz[*c*,*d*]indole from its salt 4, because this base oxidised readily. This contradicted the literature,[8] where 2-methylbenz[*c*,*d*]indole is described as a stable product (m p 290 °C)

Attempts were made to confirm the data of Fedotova *et al* [8] by other means The product obtained with good yield by treatment of a solution of benzylidene-α-naphthylamine in ethanol with catalytic amounts of hydrochloric acid has been reported by Letunov and Soldatova to be 2-phenylaza-acenaphthene.[10] This gives 2-phenylbenz[*c*,*d*]indole, described by Fedotova *et al*, by dehydrogenation. However, the solvent used for the crystallisation of the product is not disclosed According to our data it is not homogeneous From the p m.r evidence, none of three fractions isolated by chromatography of a chloroform solution on aluminium oxide is consistent in properties with 2-phenylaza-acenaphthene.

Packer and Smith[11] have suggested on the basis of mass spectrometry data, absorption spectrum and chemical properties, that the red–violet dye obtained in 3 5% yield by treatment of naphthostyril with methylmagnesium iodide has the structure (**6**; R = H) However, the elementary analysis was not quite satisfactory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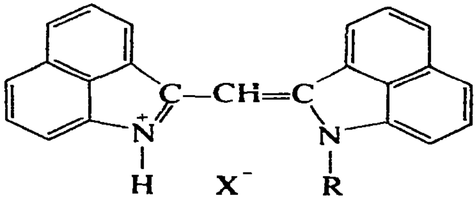
R=H.CH$_3$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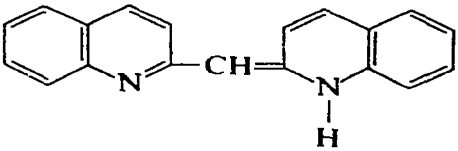
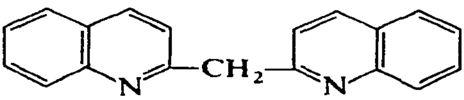
We obtained this dye in analytically pure state with 80% yield by interaction of salts **1** and **4**, to give an unambiguous product The absorption spectra of dye (**6**; R = H), its salt (**7**, R = H) and its complex with zinc acetate, given by Packer and Smith[11] and determined by us, coincide

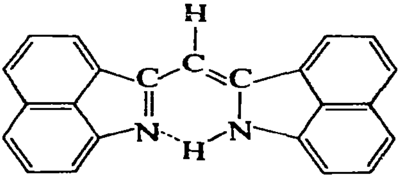
Formally, **6** is analogous to diquinolylmethanes which exist in two tautomeric forms,[12] the coloured form **a** with a mesomeric chromophore system, and the colourless one **b** stabilised by two quinoline nuclei with a large resonance energy.


a


b

The formation of the colourless form of the benz[*c*,*d*]indole 12-π-electronic system seems to be improbable This suggestion may be confirmed by the close values of extinction for the dye (**6**, R = H) and its methyl derivative (**6**, R = CH$_3$), the latter is unable to exist in colourless form (Fig 1).

As in the case of the coloured forms of diquinolyl-2-methanes,[12] the compound (**6**, R = H) is most probably characterised by a *cis*-structure with an intramolecular H-bond



The absence of the NH-bond in the i r. spectrum of the dye (**6**; R = H) may be caused by this circumstance. The pronounced similarity of rather wide absorption

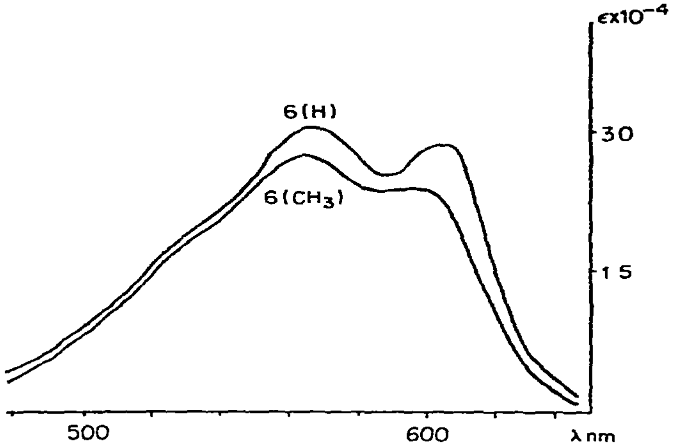


Fig 1 Absorption spectra of dyes (6. R = H CH$_3$) in benzene

bands of the dyes (6. R = H, CH$_3$) (Fig 1) indicates an electronic asymmetry of their chromophores, i e the non-equivalence of the NH-bands in the molecule (6, R = H)

Unlike the dye (6. R = H), its salts (7. R = H) possess a symmetrical electronic density distribution in the chromophores The result is a deeper colour as well as considerable narrowing of the absorption band (Fig 2)

Whereas the dyes of structure 6 show similar absorption bands and intensities,

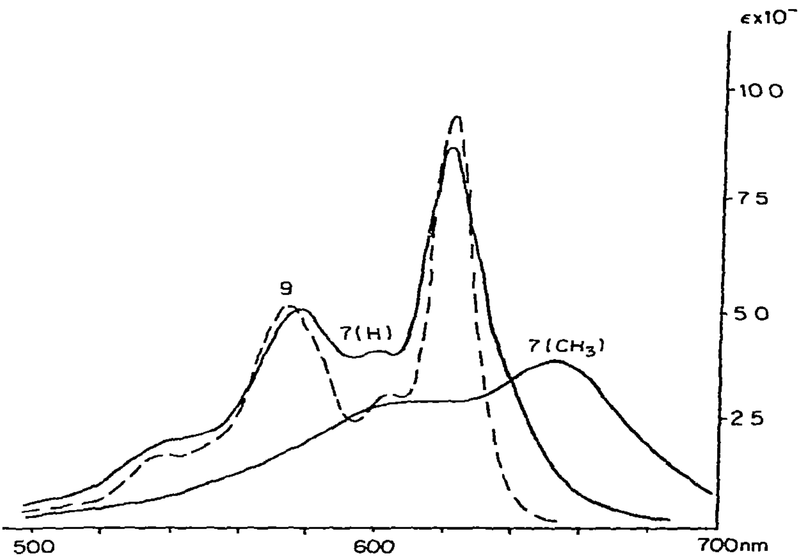
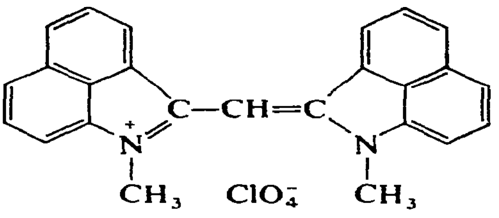


Fig 2 Absorption spectra of dyes (7 R = H, CH$_3$) in methanol and 9 in benzene

their salts (7; R = H, CH_3) differ strongly in these respects (Fig. 2). The bathochromic shift of the broad absorption band of the salt (7; R = CH_3), relative to that of the salt (7; R = H), is caused by steric hindrance to the planarity of its chromophore arising from the replacement of a hydrogen atom by a methyl group. A similar effect has been observed with dipyrrylmethenes (Brunings–Corwin effect).[13] The absorption spectrum of (7; R = CH_3) resembles that of dye 8 (λ_{max} 645 nm, ε 3·73 × 10^4),[14] where strong steric hindrance is certain.

The planarity of the molecule of (7, R = H) is confirmed by the complete analogy in the shape of the absorption band of this salt and that of the dye 9 (Fig. 2) which has entirely fixed planar structure.



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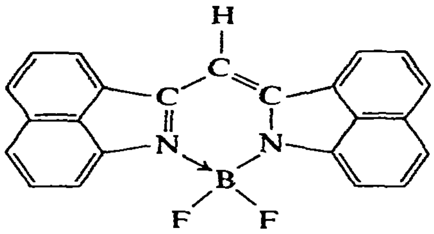

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It should be noted that absorption spectra of both compounds (Fig. 2), in addition to one vibration frequency progression (Δν 1370 cm^{-1}), display the first member of the other one (Δν 540 cm^{-1}). A similar spectral pattern has been previously observed for dyes only at very low temperatures.[15]

2. EXPERIMENTAL

2.1 *2-(2,2-Dimethyl-4,6-dioxo-1,3-dioxane-5-yliden)(1H)benz*[c,d]*indole* (3)

The mixture of 1 (16·4 g, 0·05 mol), 2 (14·4 g, 0·1 mol) and sodium acetate (8·2 g, 0·1 mol) in absolute ethanol was kept for one hour at 50 °C. The residue after cooling was separated, washed with water and dilute ethanol (1 : 1, v/v). Yield 13·8 g (94 %), m.p. 223 °C (C_6H_6), λ_{max} 453 nm, ε, 1·8 × 10^4 (C_6H_6).

Calculated for $C_{17}H_{13}NO_4$ (%): C 69·15, H 4·41, N 4·75. Found: C 68·78, 68·49; H 4·42, 4·39; N 4·72, 4·77.

2.2 *2-Methylbenz*[c,d]*indole perchlorate* (4)

The mixture of 3 (2·95 g, 10 mmol), acetic acid (25 ml) and 50 % perchloric acid was boiled until no more carbon dioxide was evolved (about 30 min). The residue after cooling was separated. Yield 2·34 g (87 %), m.p. 181 °C dec. (1 % $HClO_4$).

Calculated for $C_{12}H_9N\cdot HClO_4$ (%): C 53·83; H 3·74, Cl 13·27. Found: C 53·77, 53·94; H 4·10, 3·99; Cl 13·14, 13·06.

2.3 *2-[(4-Dimethylaminophenyl)ethenyl]benz*[c,d]*indole perchlorate* (**5**; *R* = *H*)

This was obtained (81 %) from **4** with excess *p*-dimethylaminobenzaldehyde in boiling acetic anhydride, m.p. 300 °C dec.

Calculated for $C_{21}H_{18}N_2\cdot HClO_4$ (%) Cl 8·91, N 7·03. Found Cl 8·82, 8·71; N 7·09, 7·24

2.4 *2-[(Benz*[c,d]*indole-2*(1H)*-ylidene)methyl]benz*[c,d]*indole* (**6**, *R* = *H*) *and its perchlorate* (**7**, *R* = *H*, *X* = ClO_4)

The mixture of **4** (1·61 g, 6 mmol), **1** (1·96 g, 6·5 mmol) and pyridine (12 ml) was boiled for 45 min. The salt **7** residue was washed with ethanol after cooling. Yield 2·35 g (94 %), m.p. 250 °C dec., λ_{max} 623 nm, ε 8·5 × 10^4 (CH_3OH).

Calculated for $C_{23}H_{14}N_2\cdot HClO_4$ (%) N 6·69. Found. N 6·31, 6·32

Neutral aqueous sodium diaminoethanetetra-acetate was added to the salt **7** in boiling pyridine. The residue after cooling was separated, then washed with ethanol. Yield of (**6**, R = H) 1·62 g (85 %), m.p. 180 °C (xylene) $\lambda_{1\,max}$ 567 nm, ε_1 3·2 × 10^4, $\lambda_{2\,max}$ 605 nm, ε_2 3·0 × 10^4 (C_6H_6)

Calculated for $C_{23}H_{14}N_2$ (%) C 86·79, H 4·40, N 8·81. Found C 86·80, 86·90, H 4·50, 4·71, N 8·96, 8·76

2.5 *2-[(1-Methylbenz*[c,d]*indole-2*(1H)*-ylidene)methyl]benz*[c,d]*indole* (**6**; *R* = CH_3) *and its hydrobromide* (**7**, *R* = CH_3, *X* = *Br*)

The mixture of 2-methylthiobenz[*c*,*d*]indole methyliodide[14] (0·34 g, 1 mmol), **4** (0·26 g, 1 mmol) and pyridine (2 ml) was boiled for 45 min. The salt residue was washed with ethanol, dissolved in boiling pyridine and diluted with water. Yield of **6** 0·29 g (84 %), m.p. 204 °C (xylene) $\lambda_{1\,max}$ 565 nm, ε_1 3·0 × 10^4, $\lambda_{2\,max}$ 597 nm, ε_2 2·6 × 10^4 (C_6H_6)

Calculated for $C_{24}H_{16}N_2$ (%) N 8·43. Found N 8·73, 8·64

Hydrobromide **7** was obtained by hydrobromic acid interacting with base in ethanol, m.p. 250 °C dec. (ethanol) λ_{max} 652 nm, ε 3·75 × 10^4 (CH_3OH)

Calculated for $C_{24}H_{16}N_2HBr$ (%) Br 19·37. Found: Br 19·40

2.6 *2-[(1-Difluoroborylbenz*[c,d]*indole-2*(1H)*-ylidene)methyl]benz*[c,d]*indole* (**9**)

The mixture of (**7**, R = H) (0·3 g, 1 mmol), benzene (10 ml), triethylamine (0·32 g, 3·2 mmol) and $BF_3\cdot O(C_2H_5)_2$ (0·23 g, 2 mmol) was boiled for 10 min, then the residue was separated, washed with water and ethanol. Yield 0·29 g (87 %), m.p. 300 °C dec. (DMSO) λ_{max} 622 nm, ε 9·25 × 10^4 (C_6H_6)

Calculated for $C_{23}H_{13}F_2BN_2$ (%) C 75·40, H 3·55. Found: C 74·92, 74·84, H 3·66, 3·86

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