



## A chiral arylazomethyleneindoline dye †

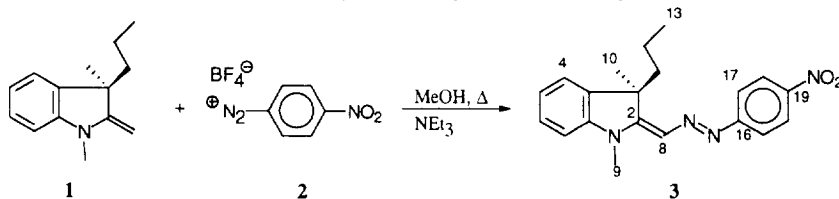
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**Abstract:** The chiral arylazomethyleneindoline dye **3** has been synthesized by coupling the chiral Fischer base **1** with *p*-nitrophenyldiazonium tetrafluoroborate **2**. The NMR spectrum of **3** reveals the existence of two conformations with a ratio of 6:1. Whereas at room temperature no photochromism is observed, *E/Z* isomerisation of the azo group of **3** is detected at  $-155^{\circ}\text{C}$ . The Cotton effect is small and is not affected by irradiation with UV or visible light. © 1997 Elsevier Science Ltd

Hydrazone dyes are of great technical importance and are produced in quantities of thousands of tons,<sup>1</sup> whereas significantly less is known about the corresponding hydrazone dye bases, the so called arylazomethyleneindoline dyes (we found less than 30 publications and patents). These dyes were first described by König in 1924.<sup>2</sup> Our aim was to examine the influence of a chiral indolyl group on the *E/Z*-isomerization of the azo group—perhaps these dyes could be useful as chiroptical switches.<sup>3</sup>

Coupling of the chiral Fischer-base **1**<sup>4</sup> with the *p*-nitrodiazonium salt **2**<sup>5</sup> was effected in the presence of triethylamine, with the azo dye **3** precipitating from the reaction mixture as greenish crystals.<sup>6</sup> The e.e. of the chiral Fischer base (and of the arylazomethyleneindoline dye) was estimated to be  $\geq 80\%$ .<sup>4</sup>



The  $^1\text{H-NMR}$  spectrum of **3** in  $\text{CDCl}_3$  at  $24^{\circ}\text{C}$  reveals the existence of two isomers with a ratio of 6:1, as estimated from the integrated area of the  $\text{N-CH}_3$  groups.

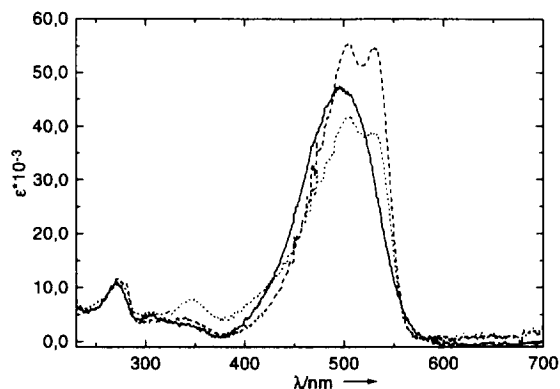
The broad unstructured absorption around 497 nm ( $\epsilon=47,000$ ) shows no photoisomerization when irradiated with UV (254 nm) or visible light at  $0^{\circ}\text{C}$  (Figure 1). Upon cooling to  $-155^{\circ}\text{C}$  this band is shifted bathochromically and split into two peaks with maxima at 502 and 535 nm respectively. When submitted to yellow light ( $>530$  nm) these bands are reduced to 2/3 of their intensity; a new band at 345 nm and a shoulder at 450 nm appear instead. Irradiation with UV light restores the original spectrum, an indication of photochromism at low temperature. Both the bathochromic shift and the photochromism found at low temperature are comparable to those found in 4-dimethylamino-4'-nitroazobenzene,<sup>7</sup> probably a consequence in both systems of the preponderance of the bipolar contribution.

The circular dichroic (CD) spectrum of **3** (Figure 2) shows only a weak unstructured band around 500 nm ( $\Delta\epsilon=+1$ ) at  $0^{\circ}\text{C}$ , which becomes slightly stronger at low temperature ( $\Delta\epsilon=+3$  at  $-155^{\circ}\text{C}$ ). No change of the CD spectrum is observed after irradiation with visible or UV light.

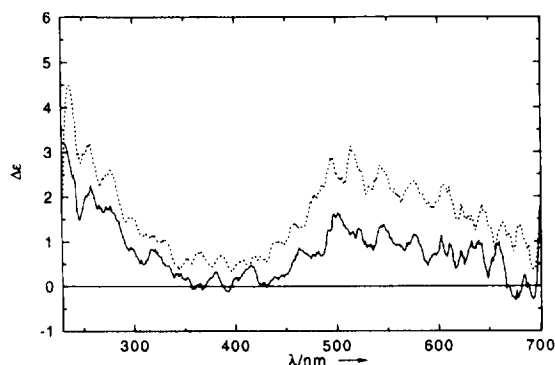
We assign this weak CD absorption to an essentially planar chromophore,<sup>8</sup> regardless of the configurations adopted by the (formal) double bonds. In solution, and disregarding the bipolar

† Dedicated to Prof. Dr D. Döpp on the occasion of his 60th birthday.

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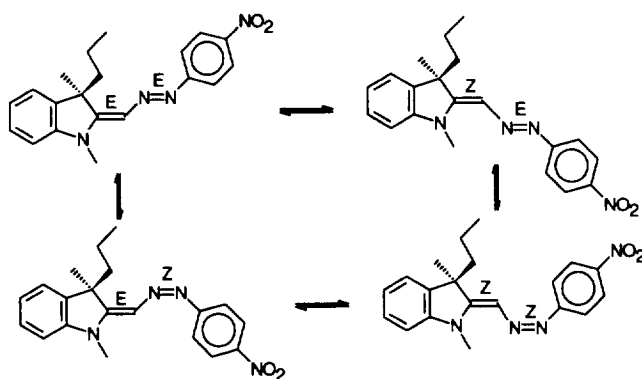


**Figure 1.** UV/Vis spectra of **3** in ethanol/methanol 4:1;  $c=6.1 \cdot 10^{-5}$  M. (—), 0°C; (---), -155°C, after irradiation with UV; (···), -155°C, after irradiation with visible light.



**Figure 2.** CD spectra of **3** in ethanol/methanol 4:1;  $c=6.1 \cdot 10^{-5}$  M. (—), 0°C; (···), -155°C.

mesomeric structures, four different conformations of the arylazomethyleneindoline dye may be envisaged:



In order to decide which of these conformations are preferred a ROESY experiment was performed at 24°C in  $\text{CDCl}_3$ . The only cross peaks observed for the methine proton H-8 involves the N- $\text{CH}_3$  group which shows that the E-conformation at the C,C double bond is favored. In addition the absence of any NOE between H-8 and an arylproton (H-17), which would be expected for the Z-conformation at the azo group, establishes that the major isomer present is E,E-**3**. Several cross peaks with the same phase as the diagonal peaks (for example between the N- $\text{CH}_3$  groups of the isomers) indicate a

fast equilibrium. This finding is confirmed by a dynamic NMR experiment: at  $-50^{\circ}\text{C}$  the equilibrium between the two conformers, which was 6:1 at RT, is now 11:1 instead, with the Z,E-conformation attributable to the minor isomer. A ratio of 10:1 for the two isomers is typical if the methylene double bond is further substituted.<sup>9</sup>

We attribute the observed changes in the UV/Vis spectra at low temperature to E/Z isomerism of the azo group (see above). Presumably because of the nearly planar geometry of the chromophore in all four conformers no change in intensity or sign of the CD absorption is observed after photoisomerization.

Further synthetic work on chirally substituted arylazomethyleneindoline dyes, with possibly larger Cotton effect, is in progress.

### Acknowledgements

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### References

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6. (+)-(3R)-2-[(4'-Nitro-benzylazo)-methylene]-1,3-dimethyl-3-propyl-indoline (**3**): 200 mg (1.3 mmol) p-Nitrophenyldiazoniumtetrafluoroborate **2**<sup>5</sup> and 220 mg (1.1 mmol) of the Fischer base **1**<sup>4</sup> are dissolved in 15 ml of abs. methanol and heated to  $60^{\circ}\text{C}$  with stirring. To this solution 0.15 ml (1.3 mmol) of triethylamine are added and stirred at  $60$ – $65^{\circ}\text{C}$  for 4.5 h. After cooling to room temperature 30 ml of water are added and the mixture is allowed to stand for 16 h at  $4^{\circ}\text{C}$ . The resulting greenish crystals are separated, washed with distilled water and recrystallized from ethanol/water and finally from methanol. Yield 120 mg (31%); mp.  $111$ – $118^{\circ}\text{C}$ ;  $\alpha_{365}^{23} = +790$  ( $c=0.00215$ , ethanol/methanol 4:1);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta=0.62$ – $0.73$  (m, 4H, 13-H, 12<sub>A</sub>-H), 0.95–1.03 (m, 1H, 12<sub>B</sub>-H), 1.76 (s, 3H, H-10), 2.01–2.07 (m, 1H, H-11<sub>A</sub>), 2.49–2.55 (m, 1H, H-11<sub>B</sub>), 2.42 (s, 3H, H-9), 6.94 (d,  $^3J=7.8$  Hz, 1H, Indole-H), 7.12–7.15 (m, 1H, Indole-H), 7.30–7.34 (m, 2H, Indole-H), 7.58 (s, 1H, H-8), 7.70 (dd,  $^3J=9.2$  Hz,  $^4J=2.1$  Hz, 2H, H-17), 8.29 (dd,  $^3J=9.2$  Hz,  $^4J=2.1$  Hz, 2H, H-18);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta=14.2$  (C-13), 18.0 (C-12), 28.8 (C-10), 30.1 (C-9), 44.8 (C-11), 108.2 (d), 121.1 (d), 122.5 (d), 123.1 (d), 123.3 (d), 125.0 (d), 128.0 (d), 138.7 (s), 144.5 (s), 145.4 (s), 158.4 (s), 168.5 (signals of the major isomer only); MS (EI, 70 eV):  $m/z=350$  (46,  $\text{M}^+$ ), 321 (46), 213 (19), 187 (79), 170 (34), 158 (100); calcd.: C 68.55, H 6.33, N 15.99, found: C 68.48, H 6.35, N 15.95.
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