

**SYNTHESIS, CRYSTAL STRUCTURE AND LIGHT ABSORPTION OF
VINYLOGOUS *N,N'*-DIALKYLINDIGOS¹**

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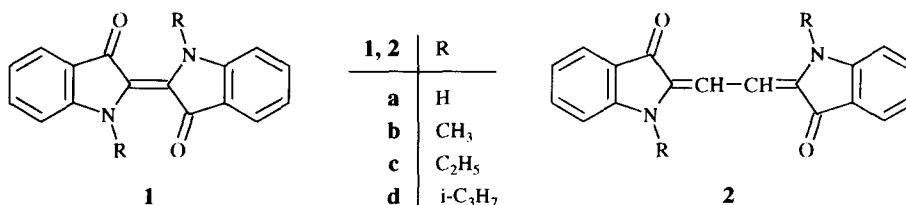
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Abstract: The base catalyzed *N,N'*-dialkylation of the vinylogous indigo dye *cis-cis*-**2a** proceeds with concomitant isomerization and yields *cis-trans*-**2b,c** as minor, and *trans-trans*-**2b,c,d** as major products. Upon exposure to light, *cis-trans*-**2b,c** isomerizes to *trans-trans*-**2b,c**. According to an X-ray analysis, *trans-trans*-**2c** and *trans-trans*-**2d** are planar. However, due to the different configurations of **2a** and **2b-d**, the light absorption data of **2a-d** cannot be used to quantify the inductive effects of the alkyl groups.
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Introduction

We recently reported² on the crystal structure and light absorption of *N,N'*-dimethylindigo **1b** and ascribed the remarkable bathochromic shift of its longest wavelength absorption maximum as compared to **1a** [$\Delta\lambda_{\max} = 50.5$ nm (CHCl₃)] to a Brunings-Corvin effect,³ i.e. a torsion of the central double bond caused by steric interaction of the methyl and the carbonyl groups. Indeed, according to the crystal structure data, this torsion amounts to 26° and is accompanied by a slight but significant pyramidalization of the carbon atoms of the central double bond, the nitrogen atoms, and the carbon atoms of the carbonyl groups. Whether, and if true, to what extent an inductive effect was operative could not be clarified.

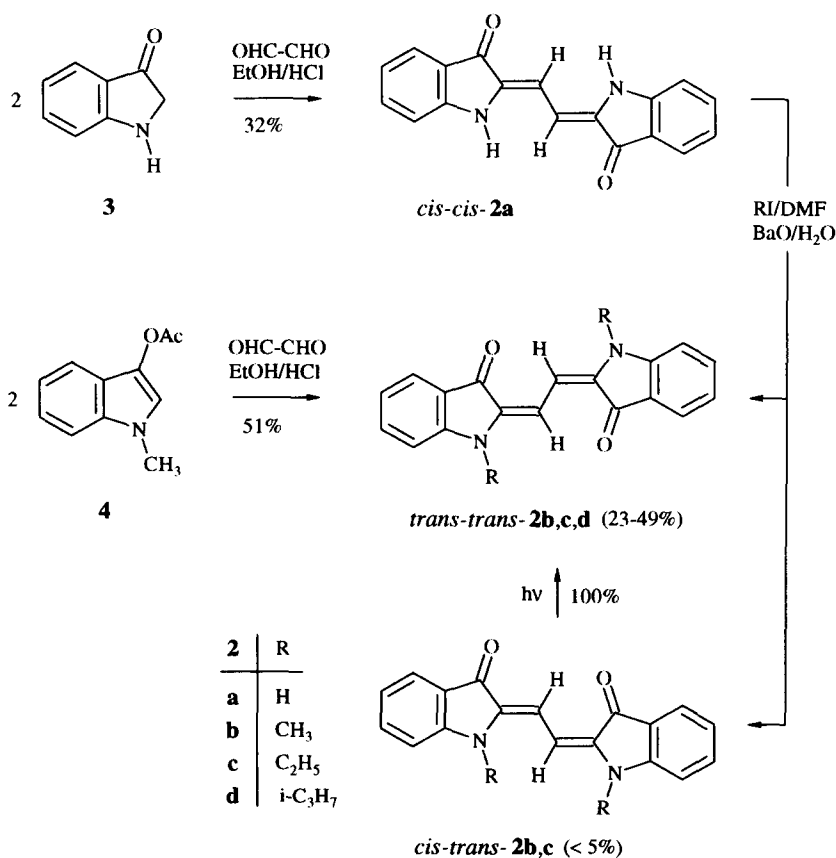


We now report on the synthesis, structure and light absorption of the vinylogous *N,N'*-dialkylindigos **2b-d** in an approach to quantify the inductive effects not only in **1b**, but also in **1c**⁴ and **1d**.⁴ Our approach was based on the expectation that **2a-d** would be both stereochemically identical and planar, so that an eventual bathochromic shift of the longest wavelength absorption maxima of **2b-d** as compared to **2a** could be ascribed to

pure inductive effects also present in **1b-d**. As will be seen from what follows, these expectations were only partially fulfilled.

Syntheses

For the synthesis of **2b-d**, we first prepared the parent compound **2a** by an acid catalyzed condensation of indoxyl (**3**) with glyoxal as described by Friedländer and Risse.⁵ **2a** is very sparingly soluble in all organic solvents and ¹H NMR, ¹³C NMR and ¹³C-¹H correlation spectra required for a configurational assignment could only be obtained from solutions in dimethyl sulfoxide-*d*₆. As indicated by the appearance of a single resonance for the vinylic protons ($\delta = 6.80$, s, 2H) and the corresponding carbon atoms ($\delta = 104.31$), **2a** was symmetrical and stereochemically pure. However, at this stage of the investigations, a decision between a *cis-cis* and a *trans-trans* configuration could not yet be made.



For the dialkylations of **2a**, we followed the protocol of Kuhn and Trischmann⁶ for the dimethylation of **1a** and reacted **2a** with a large excess of the appropriate alkyl iodide in the presence of base. In this way, methyl

and ethyl iodide delivered both a configurationally stable and unstable *N,N*-dialkylated product, while isopropyl iodide yielded only a stable one. In all cases, the isomers were separated by chromatography on silica gel in chloroform while being protected from light. During elution of the configurationally unstable isomers, a photoisomerization to the corresponding stable isomers was observed. This isomerization was provoked even by diffuse daylight, could be followed by UV/VIS spectroscopy, and was complete within minutes (Figure 1). Interestingly, acid catalyzed condensation of *N*-methyl-*O*-acetyl-indoxyl (**4**) with glyoxal yielded only the stable isomer of **2b**.

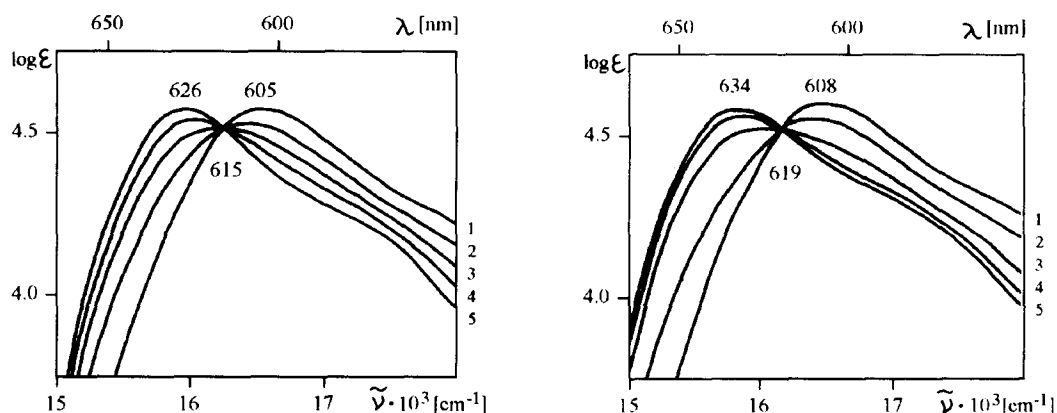


Figure 1. Photoisomerization of *cis-trans*-**2b** (λ_{\max} 605 nm, left) and *cis-trans*-**2c** (λ_{\max} 608 nm, right) to the corresponding *trans-trans*-configured isomers in chloroform. In both cases, the first spectrum was registered immediately after elution of the unstable isomer. Afterwards, the probes were subjected for 2.5 (**2b**) and 1.5 min (**2c**), respectively, to diffuse daylight until the next spectrum was taken. After registration of the last spectrum, no further change was observed.

The configurationally stable isomers crystallized from ethanol as bronze needles, Fp 285–286 (**2b**), 259–260 (**2c**) and 212–214°C (**2d**), respectively. As in the case of **2a**, their ^1H NMR, ^{13}C NMR and ^1H - ^{13}C correlation spectra indicated a symmetrical species. However, this time the resonances for the vinylic protons [δ = 8.03, s, 2H (**2b**), 8.12, s, 2H (**2c**), 8.43, s, 2H (**2d**)] and the corresponding carbon atoms [δ = 111.68 (**2b**), 111.66 (**2c**), 113.30 (**2d**)] were shifted to extremely low field. It thus turned out, that the configuration of **2a** was *cis-cis*, and the configuration of the stable isomers of **2b-c** was *trans-trans*. The configurational assignment of the unstable isomers as *cis-trans* resulted from the fact that the ^1H NMR spectrum of a sample enriched in the unstable isomer of **2b** showed two doublets for the vinylic protons [δ = 6.82, d, J = 14 Hz, 1H and 8.08, d, J = 14 Hz, 1H] at chemical shifts nearly identical with those of the corresponding protons in *cis-cis*-**2a** and *trans-trans*-**2b**, respectively.

Taking into account, that the strength of the nonbonding interactions within a six-membered arrangement follows the order alkyl-hydrogen > oxygen-hydrogen > hydrogen-hydrogen, the preference of **2a** and **2b-d** for a *cis-cis* and a *trans-trans* configuration, respectively, could have been expected. However, the mechanism of the configurational change during the alkylations of **2a** is less obvious. As all reactions were performed in the dark, a photochemical isomerization of already alkylated products, as with *cis-trans*-**2b,c**, may be excluded. We there-

fore believe that the isomerizations are initiated by a deprotonation of an amino group leading to a resonance stabilized anion with diminished rotational barriers around the formal double bonds and are terminated by a readjustment of the stereochemistry in favour of sterically less demanding *trans* relationships during the alkylation step.

Crystal Structures

Having established the configurations of **2a** and the stable isomers of **2b-d** as *cis-cis* and *trans-trans*, respectively, we tried to determine their molecular structures next. However, albeit different techniques and a large number of solvents were tested, it was only with *trans-trans-2c* and *trans-trans-2d*, that suitable crystals for an X-ray analysis could be obtained: in the case of **2c** by diffusion of pentane into a solution in chloroform, and in the case of **2d** by diffusion of water into a solution in acetic acid. In the last case, the sample crystallized with two moles of acetic acid.

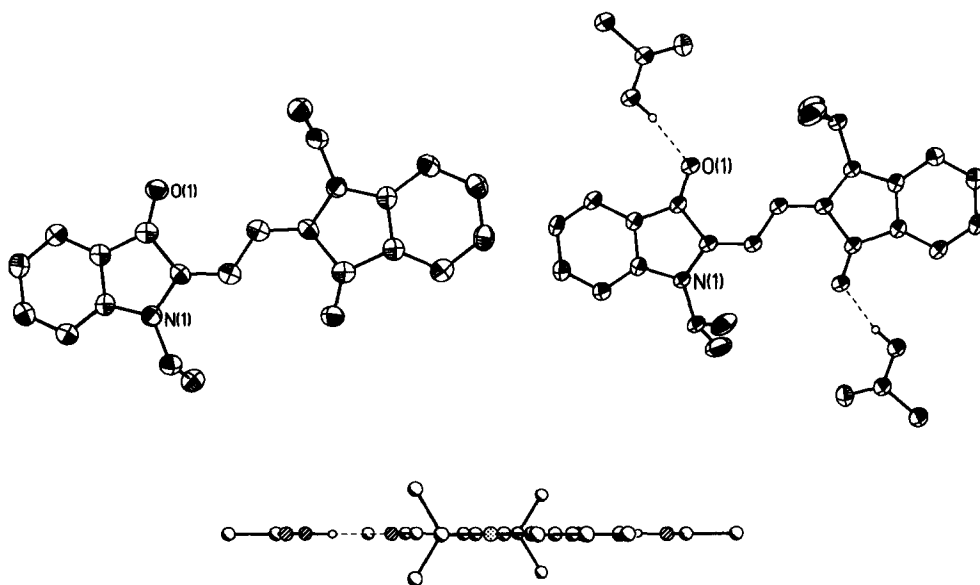


Figure 2. Crystal structure of *trans-trans-2c* (left) and *trans-trans-2d* (right) with 50% probability ellipsoids, and view perpendicular to the crystallographic y-axis of *trans-trans-2d* (bottom).

Trans-trans-2c crystallizes in the monoclinic space group $P2_1/n$ with half a molecule in the asymmetric unit, the rest of the molecule is generated by the inversion center. *Trans-trans-2d* crystallizes in the monoclinic space group $C2/m$ with a quarter of **2c** and a half molecule of acetic acid in the asymmetric unit. The rest of the molecule and a second molecule of acetic acid are generated by the mirror and the twofold axis. The acetic acid molecules are coordinated to the O atoms of **2c** via a hydrogen bond.

On the contrary to what had been found with **1b**, all non-hydrogen atoms of *trans-trans-2c* and *trans-trans-2d*, with the exception of the methyl-C atoms of the N-alkyl substituents, form a perfect plane. The methyl-C atoms deviate from this plane pairwise in opposite direction and point to the butadiene units. The bond lengths and bond angles of the ring systems match those of **1b** closely. As compared to butadiene (1.349 Å),⁷ the double bonds in **2c** (1.362 Å) and **2d** (1.358 Å) are elongated. However, for cross-conjugated systems as in **2c** and **2d** this would have been expected. Plots of the crystal structures are given in Figure 2.

Light Absorption Data

As already pointed out, a quantification of the inductive effects in **2b-c** and its use to differentiate between the influence of steric and inductive effects to the light absorption of **1b-c** was tied to the condition that **2a-c** are both stereochemically identical and planar. Unfortunately, the stereochemistry of **2a** and **2b-d** turned out to be different. Therefore, albeit *trans-trans-2c* and *trans-trans-2d* are planar, and *trans-trans-2b* and *cis-cis-2a* may be taken as planar, a comparison of the longest wavelength absorption maxima of *cis-cis-2a* and *trans-trans-2b,c,d* (Table 1) is hampered by the fact that the influence of their configuration cannot be quantified.⁸

The situation with *cis-trans-2b,c* is even worse. In these cases the fast isomerization to *trans-trans-2b,c* indicates a strong steric interaction between the alkyl group and a vinylic proton in the *cis*-configured part and hence a nonplanar structure. As the energetically most favourable way to minimize the interactions is a torsion around the central single bond, a hypsochromic shift of the longest wavelength absorption maxima as compared to hypothetically planar species should result. Therefore, the observed hypsochromic shifts as compared to *trans-trans-2b,c* (Table 1) cannot be attributed to a configurational change alone.

Table 1. Longest wavelength absorption maxima of **2a-d**: (a) in CHCl₃, (b) in DMSO.

2	λ_{\max} [nm] (log ϵ)					
	<i>cis-cis</i>		<i>cis-trans</i>		<i>trans-trans</i>	
	(a)	(b)	(a)	(b)	(a)	(b)
a	597 (-)	593 (4.43)				
b			605 (4.57)	—	626 (4.57)	634 (4.59)
c			608 (4.60)	—	634 (4.58)	638 (4.57)
d					638 (4.56)	642 (4.56)

Obviously, the dilemma is twofold: to compare *cis-cis-2a* and *trans-trans-2b,c,d* means to compare compounds with different configurations, and to compare *cis-trans-2b,c* with either *cis-cis-2a* or *trans-trans-2b,c* means to compare compounds with different configurations, and nonplanar and planar structures. In no case, the observed shift differences may be attributed to pure inductive effects. Therefore, a quantification of the inductive effects in *trans-trans-2b-d*, and hence in **1b-d**, has to await for a synthesis of *trans-trans-2a*.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 225 spectrophotometer. UV/VIS spectra were obtained with a Cary Instruments spectrometer model 14. ^1H NMR, ^{13}C NMR and ^{13}C - ^1H correlation spectra were measured with a Varian VXR 200 or VXR 500 or a Bruker AMX 300 spectrometer. For standards other than TMS the following chemical shifts were used: $\delta_{\text{H}}(\text{CHCl}_3) = 7.24$ ppm, $\delta_{\text{H}}([\text{D}_5]\text{-DMSO}) = 2.49$ ppm, $\delta_{\text{C}}(\text{CDCl}_3) = 77.00$ ppm, $\delta_{\text{C}}([\text{D}_6]\text{-DMSO}) = 39.50$ ppm. Mass spectra were determined with a Varian MAT 311 A or 701 instrument operated at 70 eV. R_f values are quoted for Macherey & Nagel Polygram SIL G/UV254 plates. Melting points were observed on a Reichert microhotstage and are not corrected.

α,β -Bis(3-oxo-indolinyliden-2)-ethane (2a): To a solution of **3** (20.0 g 150 mmol) in ethanol (350 ml) was added aqueous glyoxal (30% w/w, 14.5 g, 75 mmol) and concentrated hydrochloric acid (10 ml) and the mixture was heated for 1.5 h to reflux. After cooling, the mixture was filtrated and the residue was first washed with hot water and then with ethanol until the colour of the filtrate was light-violet. The yield of the remaining **2a** amounted to 7.0 g (32%). Blue-violet powder. IR (KBr): C=O 1658 cm^{-1} (broad). UV/VIS λ_{max} [nm] (log ϵ): DMSO: 593, 331 (4.43, 4.30). ^1H -NMR (300 MHz, $[\text{D}_6]$ -DMSO, $[\text{D}_5]$ -DMSO int): $\delta = 6.80$ (s, 2H), 6.91 (t, J = 8 Hz, 2H), 7.02 (d, J = 8 Hz, 2H), 7.45 (t, J = 8 Hz, 2H), 7.55 (d, J = 8 Hz, 2H), 10.58 (s, 2H). ^{13}C -NMR (125 MHz, $[\text{D}_6]$ -DMSO, $[\text{D}_6]$ -DMSO int): $\delta = 104.31, 111.79, 119.64$ (C_{tert}), 120.27 (C_{quat}), 123.98, 136.00 (C_{tert}), 138.34, 151.99, 184.63 (C_{quat}).

Dialkylation of 2a. General procedure: Protected from light, a mixture of **2a** (2.88 g, 10 mmol), DMF (50 ml), barium oxide (10.0 g), water (0.2 ml) and the appropriate alkyl iodide (160 mmol) was stirred under nitrogen for 13 (**2b,c**) and 19 h (**2d**), respectively. During this time, the colour of the reaction mixture changed from violet over blue to green-blue. The mixture was diluted with chloroform (25 ml) and filtered, and the residue was washed with chloroform until the filtrate was colourless. The combined filtrates were washed with water, saturated sodium thiosulfate, and water. The solution was dried (Na_2SO_4) and concentrated on a rotary evaporator to yield the crude *N,N'*-dialkylated products.

***N,N'*-Dimethyl- α,β -bis(3-oxo-indolinyliden-2)-ethane (2b):** The crude product (2.97 g) was extracted with chloroform (250 ml) and filtered from undissolved material (290 mg). Protected from light, the filtrate was chromatographed on silica gel (0.08-0.20 mm) in chloroform [column 70 x 7.5 cm; R_f 0.16 (*trans-trans-2b*), 0.06 (*trans-cis-2b*)] to yield 940 mg (30%) of pure *trans-trans-2b* and 38 mg (1%) of nearly pure *trans-cis-2b*. During elution of the latter, several probes were taken and the isomerization to *trans-trans-2b* documented by UV/VIS spectroscopy. ***trans-trans-2b*:** Bronze needles from ethanol, Fp 285-286°C (subl. 250°C). IR (KBr): C=O 1654 cm^{-1} . UV/VIS λ_{max} [nm] (log ϵ): CHCl_3 : 626, 337 (4.57, 4.58), DMSO: 634, 337 (4.59, 4.58). ^1H -NMR (300 MHz, CDCl_3 , CHCl_3 int): $\delta = 3.36$ (s, 6H), 6.82-6.90 (m, 4H), 7.43 (t, J = 8 Hz, 2H), 7.64 (d, J = 8 Hz, 2H), 8.03 (s, 2H). ^{13}C -NMR (50 MHz, CDCl_3 , CDCl_3 int): $\delta = 28.82$ (C_{prim}), 108.88, 111.68, 119.54 (C_{tert}), 121.56 (C_{quat}), 124.47, 135.53 (C_{tert}), 138.08, 151.62, 185.67 (C_{quat}). MS m/z 316 (M^+ , 100), 288 (24), 287 (48), 158 (16). Anal. calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$: C, 75.92; H, 5.10; N, 8.85. Found: C, 75.85; H, 5.17; N, 8.97. ***trans-cis-2b*:** Above 220°C, thermal isomerization to *trans-trans-2b*, Fp 285-286°C. IR (KBr): C=O 1662 cm^{-1} . UV/VIS λ_{max} [nm] (log ϵ): CHCl_3 : 605 (4.57); isosbestic point: 615 (4.50). ^1H -NMR (300 MHz, $[\text{D}_6]$ -DMSO, $[\text{D}_5]$ -DMSO int): $\delta = 3.40$ (s, 3H), 3.70 (s, 3H), 6.82 (d, J = 14 Hz, 1H), 8.08 (d, J = 14 Hz, 1H). The aromatic protons were covered by signals of *trans-trans-2b* and could not be specified. According to tlc, the undissolved material (290 mg) was enriched in *trans-cis-2b*.

***N,N'*-Diethyl- α,β -bis(3-oxo-indolinyliden-2)-ethane (2c):** The crude product (3.03 g) was dissolved in chloroform (200 ml), and, protected from light, chromatographed on silica gel (0.08-0.20 mm) in chloroform [column 70 x 7.5 cm; R_f 0.22 (*trans-trans-2c*), 0.09 (*trans-cis-2c*)] to yield 1.68 g (49%) of *trans-trans-2c*.

During elution of *trans-cis-2c*, several probes were taken and the isomerization to *trans-trans-2c* documented by UV/VIS spectroscopy. However, this isomerization was too fast, as to allow an isolation of *trans-cis-2c*. ***trans-trans-2c***: Bronze needles from ethanol, Fp 259–260°C. IR (KBr): C=O 1653 cm⁻¹. UV/VIS λ_{\max} [nm] (log ϵ): CHCl₃: 634, 338 (4.58, 4.58), DMSO: 638, 338 (4.57, 4.55). ¹H-NMR (300 MHz, CDCl₃, CHCl₃ int): δ = 1.32 (t, J = 7 Hz, 6H), 3.86 (q, J = 7 Hz, 4H), 6.86 (t, J = 8 Hz, 2H), 6.87 (d, J = 8 Hz, 2H), 7.43 (t, J = 8 Hz, 2H), 7.65 (d, J = 8 Hz, 2H), 8.12 (s, 2H). ¹³C-NMR (50 MHz, CDCl₃, CDCl₃ int): δ = 12.05 (C_{prim}), 36.98 (C_{sek}), 108.84, 111.66, 119.48 (C_{tert}), 121.65 (C_{quart}), 124.58, 135.50 (C_{tert}), 136.62, 150.74, 185.88 (C_{quart}). MS m/z 372 (M⁺, 100), 302 (26), 287 (33), 259 (14). Anal. calcd for C₂₂H₂₀N₂O₂: C, 76.72; H, 5.85; N, 8.11. Found: C, 76.85; H, 5.72; N, 8.24. ***trans-cis-2c***: UV/VIS λ_{\max} [nm] (log ϵ): CHCl₃: 608 (4.60); isosbestic point: 619 (4.51).

***N,N*-Diisopropyl- α,β -bis(3-oxo-indolinyliden-2)-ethane (2d)**: The crude product (1.89 g) was dissolved in chloroform (40 ml), and, protected from light, chromatographed on silica gel (0.08–0.20 mm) in chloroform [column 50 x 5 cm; R_f 0.29 (*trans-trans-2d*)] to yield 850 mg (23%) pure *trans-trans-2d*. Bronze needles from ethanol, Fp 212–214°C. IR (KBr): C=O 1653 cm⁻¹. UV/VIS λ_{\max} [nm] (log ϵ): CHCl₃: 638, 339 (4.56, 4.55), DMSO: 642, 338 (4.56, 4.54). ¹H-NMR (300 MHz, CDCl₃, CHCl₃ int): δ = 1.48 (d, J = 7 Hz, 12H), 4.48 (sept, J = 7 Hz, 2H), 6.85 (t, J = 8 Hz, 2H), 7.02 (d, J = 8 Hz, 2H), 7.40 (t, J = 8 Hz, 2H), 7.66 (d, J = 8 Hz, 2H), 8.43 (s, 2H). ¹³C-NMR (50 MHz, CDCl₃, CDCl₃ int): δ = 19.54 (C_{prim}), 46.30, 110.47, 113.30, 119.24 (C_{tert}), 122.05 (C_{quart}), 124.61, 135.22 (C_{tert}), 136.51, 150.45, 186.23 (C_{quart}). MS m/z 344 (M⁺, 100), 315 (27), 288 (17). Anal. calcd for C₂₄H₂₄N₂O₂: C, 77.41; H, 6.50; N, 7.52. Found: C, 77.51; H, 6.47; N, 7.25.

***N,N*-Dimethyl- α,β -bis(3-oxo-indolinyliden-2)-ethane (2b) from *N*-methyl-*O*-acetyl-indoxyl (4)**: To a warm solution of **4** (1.0 g, 5.3 mmol) and aqueous glyoxal (1.0 g, 30% w/w, 5.2 mmol) in ethanol (15 ml) was added conc HCl (1.5 ml), causing an instanteneous colour change from colourless over green-blue to deep-blue. The mixture was held for 5 min at 70°C and then cooled. The precipitate was suction-filtered, washed with a small amount of cold ethanol and dried to yield 425 mg (51%) of pure *trans-trans-2b* as bronze needles, Fp 284–286°C. The ¹H and ¹³C NMR data were identical with those of authentic material.

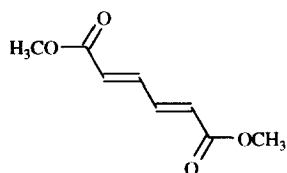
Crystal structure analyses: *trans-trans-2c*: C₂₂H₂₀N₂O₂, *Mr* = 344.40, crystal size: 0.40 × 0.30 × 0.05 mm³, monoclinic, space group *P*2₁/*n*, *a* = 10.1634(2), *b* = 6.5592(2), *c* = 12.8535(3) Å, β = 100.451(1)°, *V* = 842.65(4) Å³, *Z* = 2, ρ_{calcd} = 1.357 Mg m⁻³, *F*(000) = 364, λ = 0.71073 Å, *T* = 133 K, $\mu(\text{MoK}\alpha)$ = 0.088 mm⁻¹. Total number of reflections measured 19270, unique 1030 (*R*_{int} = 0.0765). Data/restraints/parameters: 1030/0/120, data collection range: 2.36 ≤ θ ≤ 21.97°. Final *R* indices: *R*1 = $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ = 0.0625, *wR*2 = $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ = 0.1621 on data with *I* > 2 σ (*I*) and *R*1 = 0.0709, *wR*2 = 0.1713 on all data; goodness of fit *S* = $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (n-p)]^{1/2}$ = 1.156; extinction coefficient 0.010(7); largest difference peak and hole: 0.301 and -0.283 e·Å⁻³. ***trans-trans-2d***: C₂₄H₂₄N₂O₄, + 2 C₂H₄O₂ *Mr* = 372.47 + 2 · 60.02, crystal size: 0.70 × 0.50 × 0.10 mm³, monoclinic, space group *C*2/*m*, *a* = 8.0279(2), *b* = 6.6746(1), *c* = 11.4342(2) Å, β = 101.586(1)°, *V* = 1273.07(2) Å³, *Z* = 2, ρ_{calcd} = 1.285 Mg m⁻³, *F*(000) = 524, λ = 0.71073 Å, *T* = 133 K, $\mu(\text{MoK}\alpha)$ = 0.091 mm⁻¹. Total number of reflections measured 14705, unique 1194 (*R*_{int} = 0.0879). Data/restraints/parameters: 1194/1/111, data collection range: 1.82 ≤ θ ≤ 24.71°. Final *R* indices: *R*1 = 0.0509, *wR*2 = 0.1230 on data with *I* > 2 σ (*I*) and *R*1 = 0.0598, *wR*2 = 0.1529 on all data; goodness of fit *S* = 1.114; extinction coefficient 0.004(2); largest difference peak and hole: 0.314 and -0.205 e·Å⁻³. The crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.⁹ Diffraction data were collected on a Stoe-Siemens-Huber four-circle-diffractometer coupled to a Siemens CCD area-detector at 133(2) K, with graphite-monochromated MoK α radiation (λ = 0.71073 Å), performing ϕ - and ω -scans. The structures were solved by direct methods using the program SHELXS-97¹⁰ and refined against *F*² on all data by full-matrix least squares with SHELXL-97.¹¹ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as

supplementary publication no. CCDC 133686 and CCDC 133687, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: Code + (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

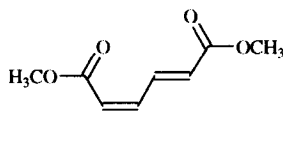
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Dedicated to Professor Martin Klessinger on the occasion of his 65th birthday

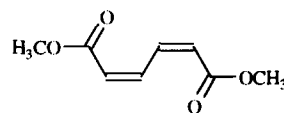
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- The only hint that the influence of the configuration on the longest wavelength absorption maxima of **2b-d** might be small is the fact that the three stereoisomeric muconic acid methyl esters **5** absorb at nearly identical wavelengths: λ_{max} [nm] (EtOH): 265 (*trans-trans*), 266 (*cis-trans*), 265 (*cis-cis*): Elvidge, J. A., Linstead, R. P., Sims, P., Orkin, B. A. *J. Chem. Soc.* **1950**, 2235-2241.



trans-trans-5



cis-trans-5



cis-cis-5

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