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NEW INDIGO CHROMOPHORES CONTAINING DISULFIDE DONOR GROUPS

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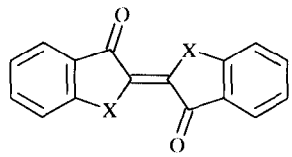
Abstract: Oxidative dimerization of a mixture of the thiolanone **5** and the dithiolanone **4** yields **2c** as chromophore of thioindigo **1c**, and **6** and **7** as chromophores of still unknown indigo dyes. As compared to **2c**, the first ionization potential of the new indigo chromophore **7** is higher, but the calculated HOMO-LUMO splitting is lower. Accordingly, its longest wavelength absorption maximum surpasses that of **2c** distinctly.

Introduction

Predicted by HMO- und PPP-calculations,[1] and confirmed experimentally,[2-4] the 22 π-electron system of the indigo dyes **1a-c** may be reduced to a 10 π-electron system as in **2a-c** without appreciable loss of colour. Thus, **2a-c** represent the basic chromophores of **1a-c** and contain them in the planar arrangement[5] and the *trans-s-cis-s-cis* configuration characteristic for **1a-c**. As a consequence, their longest wavelength absorption maxima only slightly fall short of those of the corresponding parent compounds **1a-c** (Table 1).



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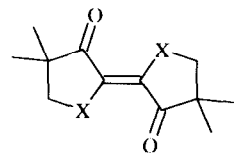

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Table 1. Longest wavelength absorption maxima of **1a-c** and **2a-c** in ethanol.

		λ_{max} [nm]		ν_{max} [cm^{-1}]	
	X	**1**	**2**	**1**	**2**
a	NH	606	480	16 600	20 800
b	Se	559	478	17 890	20 920
c	S	542	453	18 500	22 100

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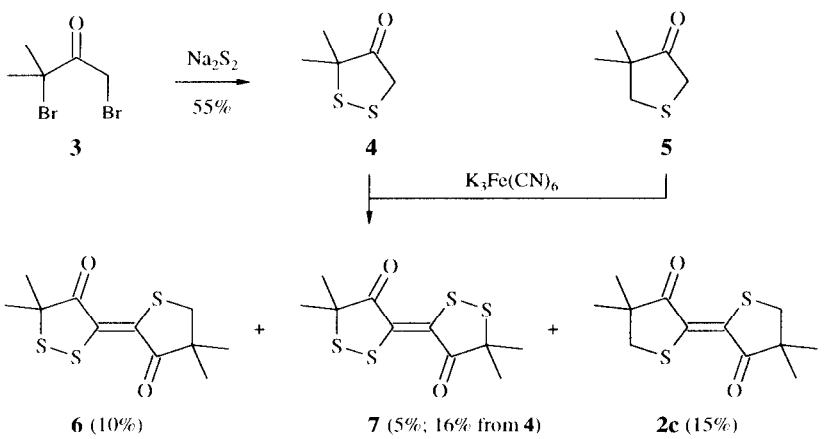
Given the fact that **2a-c** are well tailored to mimic the properties of **1a-c**, it is tempting to devise chromophores of still unknown indigo dyes by just varying the donor and/or acceptor groups. We herein report on the synthesis, structure and spectroscopic properties of two such systems derived from **2c** by incorporating one and two disulfide groups, respectively. As compared to **2c**, the resulting new chromophores **6** and **7** absorb at distinctly longer wavelengths.

Syntheses and Crystal Structures

We obtained **6** (Fp 144°C) and **7** (Fp 191°C) together with **2c**[4] by oxidative dimerization of a 1:1-mixture of 4,4-dimethyl-thiolan-3-one (**5**)[6] and 3,3-dimethyl-[1,2]dithiolan-4-one (**4**),[7] itself obtained by reaction of 1,3-dibromo-3-methyl-butan-2-one (**3**)[8] with sodium disulfide. Both compounds were separated from each other and from **2c** by column chromatography on silica gel in chloroform and crystallized from ethanol yielding crystals suitable for X-ray crystal structure analyses. These analyses revealed, that both **6** and **7** adopt the *trans-s-cis-s-cis* configuration already established for **2c**.[4] In the case of **7**, the same conclusion could have been drawn from the IR spectrum. It shows only one (antisymmetrical) carbonyl frequency at 1667 cm^{-1}.



The single-crystal X-ray structures show **6** and **7** to crystallize in the monoclinic space group $P2_1/n$ with half a molecule in the asymmetric unit. The rests of the molecules are generated by the inversion center. In the case of the asymmetric species **6** the molecule is disordered about the inversion center (occupancies 50:50) to fulfil the symmetry of the space group. In both **6** and **7** the five-membered rings adopt a half-chair conformation. These half-chairs are connected such, that the atoms of the central double bond and the adjacent carbon and sulfur atoms take part of one plane, while the peripheral carbon and sulfur atoms, and, to a smaller extent, the oxygen atoms deviate from this plane pairwise in opposite direction. As a result, **6** exhibits a pseudo inversion center, and **7** a real one. Plots of the X-ray crystal structures of **6** and **7** are given in Figure 1.

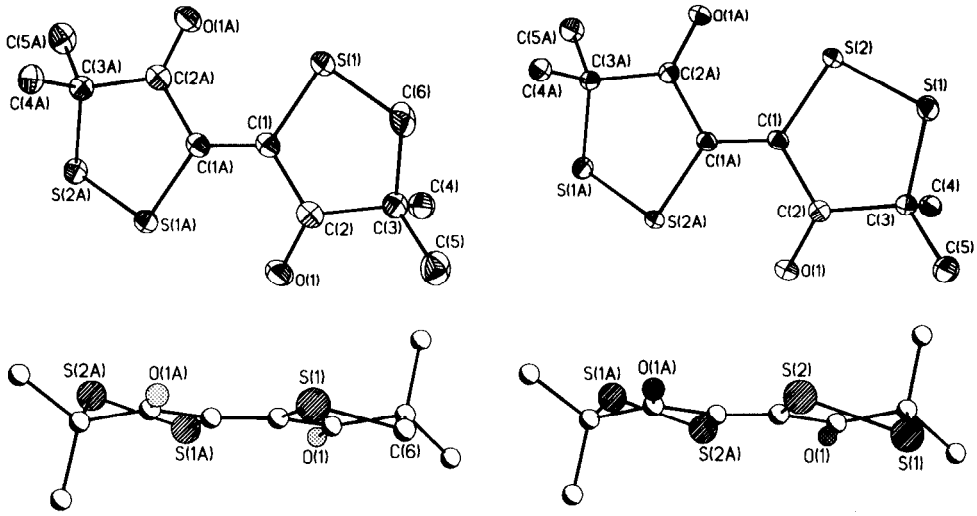


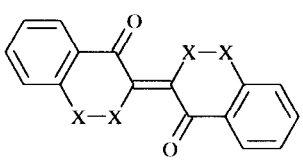
Figure 1. Crystal structure of **6** (left) and **7** (right) with 50% probability elipsoids.

UV and PE Spectroscopic Data

Most interesting with regard to a prediction of the colour of the corresponding indigo dyes is a comparison of the longest wavelength absorption maxima of **6** and **7** with those of **2a-c**[2-4] (Table 2). Independant of the solvent used, **6** and **7** absorb approximately 25 and 50 nm, respectively, at longer wavelengths than **2c**. While the longest wavelength absorption maxima of **6** reach those of **2a** and **2b**, those of **7** surpass all. It could therefore well be, that the unknown indigo dye **8a**, containing the new chromophor **7**, albeit in six-membered rings, absorbs at longer wavelengths than the classical indigo dyes **1a-c**. The same could be true for **8b**.

Table 2. Longest wavelength absorption maxima of **2a-c**, **6** and **7** in different solvents.

	λ_{max} [nm] (log ε)				
	2a	**2b**	**2c**	**6**	**7**
Cyclohexane	473 (4.05)	476 (4.17)	450 (4.13)	475 (3.76)	503 (3.74)
Ethanol	480 (3.99)	478 (4.07)	453 (4.09)	475 (3.76)	503 (3.72)
Benzene	483 (4.05)	480 (4.12)	454 (4.10)	478 (3.77)	507 (3.74)
Chloroform	487 (4.00)	482 (4.04)	458 (4.07)	481 (3.74)	510 (3.72)



8a X = S
8b X = Se

The PE spectrum of **7** is depicted in Figure 2; the relevant ionization potentials are summarized in Table 3 together with the results of quantum chemical calculations. In the low-energy region (< 11 eV), five ionization bands are found of which only one (that centred at 9.36 eV) seems to be composed of two different ionizations. Based on PM3 and B3LYP calculations, assignments are readily made. Compared to **2c**,[9,10] the first IP is raised by 0.23 eV while the second is lowered by 0.33 eV.

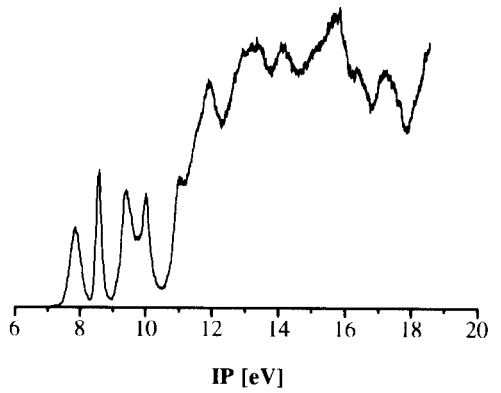


Figure 2. PE spectrum of **7**

Table 3. Vertical ionization potentials IP_v [eV] and orbital energies ε [eV] of **7**.

Ip_v exp.	PM3 -ε	B3LYP/6-31+G* -ε	IP_v[a]	Assignment
	1.74	3.21		π_6 (LUMO)
7.83	8.64	5.96	7.53	π_5 (HOMO)
8.54	9.32	6.57	8.14	π_4
9.36	10.90	7.51	9.08	π_3
9.5 sh	10.95	7.66	9.23	$n^+(O)$
9.97	11.54	8.00	9.57	$n^-(O)$
11.0	12.26	9.10	10.67	$n^-(S)$
	12.37	9.36	10.93	$n^+(S)$

[a] Calculation of first vertical *IP*: energy difference of molecule (E = -2131.51089 au) and radical cation with identical geometry (E = -2131.23399 au). Higher *IP*s: $IP_i = -\varepsilon_i + 1.57$ eV.

In accord with their low excitation energies and long-wavelength absorptions, indigoid compounds are characterized by narrow HOMO-LUMO splittings.[10] The HOMO-LUMO energy gap of **7** is calculated as 6.90 eV (PM3) or 2.75 eV (B3LYP) which is lower than that obtained for **2c** (7.40 or 3.05 eV).[10] The fact that **7** has a lower excitation energy than **2c** is reflected by the smaller HOMO-LUMO gap and can first of all be traced back to a larger stabilization of the LUMO than that of the HOMO.

EXPERIMENTAL

The PE spectrum was recorded on a UPG200 spectrometer of Leybold-Heraeus equipped with a He(I) radiation source (21.21 eV). Semi-empirical PM3[11] calculations were performed with the MOPAC93[12] program package, B3LYP[13] calculations with the program GAUSSIAN 94.[14] IR spectra were recorded on a Perkin-Elmer 225 spectrophotometer. UV/VIS spectra were obtained with a Cary Instruments spectrometer model 14. ^1H and ^{13}C NMR spectra were measured with a Varian VXR 200 or a Bruker AMX 300 spectrometer. For standards other than TMS the following chemical shifts were used: $\delta_H(CHCl_3)$ = 7.24 ppm, $\delta_C(CDCl_3)$ = 77.00 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.

3,3-Dimethyl-[1,2]dithiolan-4-one (4): A solution of sodium disulfide, prepared by heating sodium sulfide nonahydrate (48.0 g, 0.20 mol) and sulfur (6.40 g, 0.20 g atom) in ethanol (300 ml) for 1.5 h to reflux, was cooled to 30°C until a solution of **4** (48.8 g, 0.20 mol) in ethanol (150 ml) was added at such a rate that the internal temperature did not exceed 45°C (30 min). After the addition was complete, the mixture was heated for 1 h to reflux, cooled, poured into water (1.0 l) and extracted with dichloromethane (2 x 150 ml). The combined extracts were washed with water (2 x 150 ml), dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 30°C/15 torr). The residual brown oil (30 g) was fractionated in vacuo to yield 16.4 g (55%) **4** as an unpleasant smelling yellow liquid, bp 82-83°C/15 torr (lit[7a] 90-102°C/25 torr, lit[7b] 70°C/11 torr). ^{1}H NMR (300 MHz, $CDCl_3$, TMS int): 1.53 (s, 6H), 3.58 (s, 2H).^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): 23.70 (C_{prim}), 41.58 (C_{sek}), 55.70, 210.22 (C_{quart}). MS m/z 148 (100, M^+). Anal. calcd for $C_5H_8OS_2$: C, 40.51; H, 5.44. Found: C, 41.63; H, 5.74.

Trans-4,4,4′,4′-tetramethyl-[2,2′]bithiolanylidene-3,3′-dione (2c), trans-5-(4,4-dimethyl-3-oxo-thiolan-2-ylidene)-3,3-dimethyl-[1,2′]dithiolan-4-one (6) and trans-5,5,5′,5′-tetramethyl-[3,3′]bi[1,2′]dithiolanylidene-4,4′-dione (7): To a solution of potassium hexacyanoferrate (III) (39.5 g, 120 mmol) and potassium hydroxide (15.6 g, 86%, 240 mmol) in water (400 ml) was added all at once a 1:1-mixture of **4** (2.22 g, 15 mmol) and **5** (1.95 g, 15 mmol) in ethanol (40 ml) causing a slightly exothermic effect and an immediate separation of an oily solid. The mixture was heated for 10 min on a water bath and then filtered. The residue was dissolved in dichloromethane (200 ml), and the solution was washed with water (2 x 100 ml) and dried ($MgSO_4$). The solvent was distilled off on a rotary evaporator (bath temperature 30°C/15 torr) and the remaining material (2.1 g) was chromatographed on silica gel (0.05-0.20 mm) in benzene [column 80 x 5 cm; R_f = 0.72 (**7**), 0.50 (**6**), 0.26 (**2c**)] yielding 590 mg (15%) **2c**, 430 mg (10%) **6** and 240 mg (5%) **7** as orange, light-red and deep-red solids, respectively. Analytically pure samples of **2c**, **6** and **7** were obtained by crystallization from ethanol. Oxidation of pure **4** gave only **7** (16%).

2c: Fp 232-234°C (lit[4] 233-234°C). The ^{1}H NMR data were identical with literature data.[4] The ^{13}C NMR data have not yet been reported and were as follows: ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 24.33 (C_{prim}), 41.62 (C_{sek}), 45.97, 131.01, 207.36 (C_{quart}).

6: Fp 144°C (subl. 110°C). IR (KBr): C=O 1690, 1673 cm^{-1}. UV/VIS λ_{max} [mμ] (log ε): C_6H_{12}: 475, 376 sh, 358 (3.76, 3.41, 3.53), C_2H_5OH: 475, 375 sh, 357 (3.76, 3.43, 3.51), C_6H_6: 478, 377 sh, 359 (3.77, 3.44, 3.53), $CHCl_3$: 481, 377 sh, 359 (3.74, 3.42, 3.51), KBr: 495. ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.28 (s, 6H), 1.57 (s, 6H), 3.10 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 24.06, 24.30 (C_{prim}), 42.35 (C_{sek}), 46.21, 56.77, 128.66, 137.25, 201.81, 207.40 (C_{quart}). MS m/z 274 (81, M^+), 172 (100), 88 (25). Anal. calcd for $C_{11}H_{14}OS_3$: C, 48.14; H, 5.14; S, 35.05. Found: C, 47.93; H, 5.06; S, 35.30.

7: Fp 191°C (subl. 130°C). IR (KBr): C=O 1667 cm^{-1}. UV/VIS λ_{max} [mμ] (log ε): C_6H_{12}: 503, 386 sh, 367, 346, 295 (3.74, 3.02, 3.13, 3.20, 3.53), C_2H_5OH: 503, 387 sh, 364, 347, 295 (3.72, 3.02, 3.13, 3.19, 3.53), C_6H_6: 507, 386 sh, 368, 348, 296 (3.74, 3.00, 3.13, 3.20, 3.54), $CHCl_3$: 510, 386 sh, 368, 347, 296 (3.72, 2.98, 3.11, 3.20, 3.52), KBr: 553. ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.60 (s). ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 24.06 (C_{prim}), 57.31, 134.76, 201.88 (C_{quart}). MS m/z 292 (100, M^+), 190 (60), 106 (46). Anal. calcd for $C_{10}H_{12}S_4$: C, 41.07; H, 4.14; S, 43.86. Found: C, 41.03; H, 4.11; S, 44.10.

Crystal structure analyses: 6: $C_{10}H_{14}O_2S_3$, Mr = 274.40, crystal size: 0.40 × 0.40 × 0.30 mm^3, monoclinic, space group $P2_1/n$, a = 8.4162(1), b = 8.1001(9), c = 9.209(1) Å, β = 100.953(7)°, V = 616.3(1) Å^3, Z = 2, ρ_{calcd} = 1.479 Mg m^{-3}, $F(000)$ = 288, λ = 0.71073 Å, T = 133 K, $\mu(Mo_{K\alpha})$ = 0.583 mm^{-1}. Total number of reflections measured 13765, unique 1081 (R_{int} = 0.0288). Data/restraints/parameters: 1081/69/85, data collection range: 3.01 ≤ θ ≤ 25.03°. Final R indices: $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.0602$, $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma wFo^4]^{1/2} = 0.1437$ on data with $I>2\sigma(I)$ and $R1 = 0.0605$, $wR2 = 0.1438$ on all data; goodness of fit $S = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma(n-p)]^{1/2} = 1.372$; extinction coefficient 0.015(4); largest difference peak and hole: 0.453 and -0.580 e·Å^{-3}. **7**: $C_{19}H_{12}O_2S_4$, Mr = 292.44, crystal size: 0.70 × 0.50 × 0.20 mm^3, monoclinic, space group $P2_1/n$, a = 8.265(2), b = 8.228(2), c = 9.178(2) Å, β = 101.14(3)°, V = 612.4(2) Å^3, Z = 2, ρ_{calcd} = 1.586 Mg m^{-3}, $F(000)$ = 304, λ = 0.71073 Å, T = 153 K, $\mu(Mo_{K\alpha})$ = 1.495 mm^{-1}. Total number of reflections measured 10502, unique 1248 (R_{int} = 0.0366). Data/restraints/parameters: 1248/0/76, data collection range: 3.04 ≤ θ ≤ 26.37°. Final R indices: $R1$ = 0.0221, $wR2$ = 0.0578 on data with $I>2\sigma(I)$ and $R1$ = 0.0245, $wR2$ = 0.0590 on all data; goodness of fit S = 1.082; extinction coefficient 0.060(4); largest difference peak and hole: 0.398 and -0.230 e·Å^{-3}. The crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.[15] 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 $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), performing φ- and ω-scans. The

structures were solved by direct methods using the program SHELXS-97[16] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[17] 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. The disorder in **6** was modelled with the help of similarity restraints for 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 133014 and CCDC 133015, 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 Wolfgang Lüttke on the occasion of his 80th birthday

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