A Novel Intramolecular Photo-redox Reaction: Acyclic–Cyclic Interconversion between Dithiol and Disulfide in Thioindigo Derivatives

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Synthesis of new thioindigo derivatives containing SH groups at the terminal positions of the side chains, intramolecular S–S bond formation by a photo-redox reaction, and thermal bond scission due to reducing ability of the leuco form are described.

The photoreduction of indigo[1,2] and chromophores like ketones[3] which also undergo a similar type of photoreduction has been well studied. Such photoreductions occur in the presence of potential reductants, such as triethylamine. In contrast to this intermolecular photoreduction of indigo dyes we have designed a new compound to establish a photo-redox reaction that occurs intramolecularly. Such an intramolecular photo-redox reaction also provides acyclic–cyclic interconversion which differs from that of redox-switched crown ethers[4] where the interconversion was effected chemically and light was of no use.

We now report the first examples of thioindigo derivatives **3** containing thiol groups which undergo reversible reactions in which disulfide bond formation by a photo-redox reaction and bond scission in the dark occur intramolecularly. This work also provides a model for studies of photoinduced cyclisation and thermal acyclisation which may be the most suitable type of system for controlled ion transport.

The synthesis of the new thioindigo derivatives is shown in Scheme 1. Starting from dithiodisalicylic acid, 7,7′-bischlorocarbonylthioindigo **1** was prepared according to the literature.[5] Alcohols containing a thioester unit were added to the 7,7′-positions of **1** to give the thioindigo derivatives **2**. Hydrolysis of the thioester[4] units with hydrazine monohydrate followed by acidification, under nitrogen, gave the thioindigo derivatives **3**.† Hydrolysis of **2c** in air gave compound **5c**.† The products were identified by IR, NMR, UV–VIS and mass spectroscopy and elemental analysis.

Irradiation of an argon-bubbled 1,2-dichloroethane solution of compound **3c** with 550 nm light led to bleaching of the absorption bands at 534 and 316 nm with simultaneous

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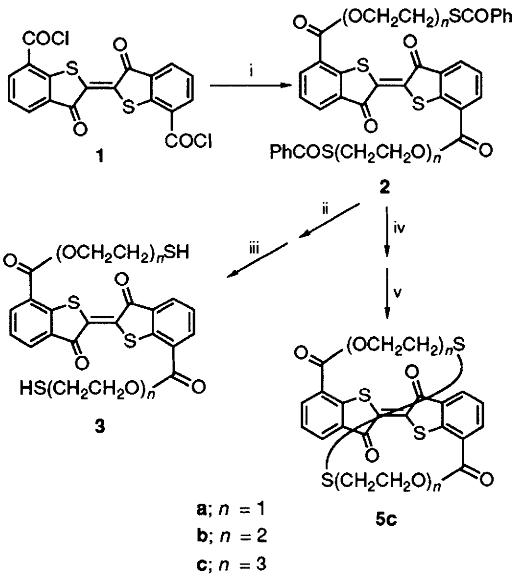
† ^{1}H NMR (300 MHz) data (δ in $CDCl_3$): **3a** 8.36 (2H, d, *J* 7.5 Hz), 8.16 (2H, d, *J* 7.5 Hz), 7.47 (2H, t, *J* 7.5 Hz), 4.60 (4H, t, *J* 6.6 Hz), 3.01 (4H, dt, *J* 8.7, 6.6 Hz) and 1.76 (2H, t, *J* 8.7 Hz); **3b** 8.36 (2H, d, *J* 7.5 Hz), 8.14 (2H, d, *J* 7.5 Hz), 7.45 (2H, t, *J* 7.5 Hz), 4.62 (4H, t, *J* 4.8 Hz), 3.93 (4H, t, *J* 4.8 Hz), 3.77 (4H, t, *J* 6.3 Hz), 2.78 (4H, dt, *J* 8.1, 6.3 Hz) and 1.64 (2H, t, *J* 8.1 Hz); **3c** 8.36 (2H, d, *J* 7.5 Hz), 8.14 (2H, d, *J* 7.5 Hz), 7.45 (2H, t, *J* 7.5 Hz), 4.62 (4H, t, *J* 4.8 Hz), 3.95 (4H, t, *J* 4.8 Hz), 3.81–3.78 (4H, m), 3.73–3.69 (4H, m), 3.63 (4H, t, *J* 6.3 Hz), 2.68 (4H, dt, *J* 8.1, 6.3 Hz) and 1.57 (2H, t, *J* 8.1 Hz).

5c 8.39 (2H, d, *J* 7.5 Hz), 8.15 (2H, d, *J* 7.5 Hz), 7.47 (2H, t, *J* 7.5 Hz), 4.68 (H, t, *J* 4.5 Hz), 3.94 (4H, br), 3.76 (4H, br), 3.64 (4H, t, *J* 4.5 Hz), 3.44 (4H, t, *J* 6.9 Hz) and 2.35 (4H, t, *J* 6.9 Hz).



Scheme 1 *Reagents and conditions*: i, $H(OCH_2CH_2)_nSCOPh$, benzene, pyridine, room temp.; ii, $NH_2NH_2{\cdot}H_2O$, MeOH–C_6H_6, reflux, N_2 (gas); iii, HCl; iv, $NH_2NH_2{\cdot}H_2O$, MeOH–C_6H_6, reflux, air; v, HCl. Yield (%): **3a**, 60; **3b**, 78; **3c**, 85; and **5c** 78.

development of new absorptions at 390 and 268 nm as shown in Fig. 1. When the photolysed solution was kept in the dark without admitting air, the visible absorption was regenerated. The rate constants for thermal reversion of **4b,c** to **3b,c** in the dark were determined spectrophotometrically by monitoring the increase in the absorption maximum at 534 nm; the thermal reversion in 1,2-dichloroethane solution at 25 °C was a first-order process. The rate constant (k) for reversion of **4b** to **3b** is $19.4 \times 10^{-5}\ s^{-1}$ ($t_{\frac{1}{2}}$ *ca.* 1 h) and that for **4c** to **3c** is $4.8 \times 10^{-5}\ s^{-1}$ ($t_{\frac{1}{2}}$ *ca.* 4 h). The linearity was generally excellent ($r > 0.999$). Isosbestic points at 280, 345 and 435 nm were maintained indicating no side reaction during irradiation, consistent with the regeneration of the diminished peaks.

Both the forward and the reverse intramolecular redox reactions are shown in Scheme 2. Compound **4** was identified by FTIR and NMR spectroscopy. The IR spectrum indicated that on photolysis the thioindigo skeletal carbonyl groups were reduced. The sharp carbonyl peak at 1657 cm^{-1} diminished and at the same time a new peak (broad) developed at 3362 cm^{-1} (hydroxy group of the leuco thioindigo). When the photolysed solution was kept in the dark without admitting air, the skeletal carbonyl groups were restored, as shown by regeneration of the peak at 1657 cm^{-1}. Similarly, the NMR spectrum of the photolysed solution showed the hydroxy proton resonance of the leuco form as a sharp peak at δ 8.88 which disappeared on addition of D_2O. All the side chain proton signals of the photolysed sample were moved towards higher field except for those due to the protons adjacent to sulfur, which shifted towards lower field. The decrease in the triplet for the thiol protons and double triplet for the methylene protons adjacent to the thiol group and development of a new triplet at lower field (δ 2.88) clearly indicate the formation of a disulfide. These IR and NMR results thus show that the terminal thiol groups reduced the skeletal carbonyl. After the irradiated had been kept in the dark for several hours the NMR spectrum was found to have exactly its original shape before irradiation. The regeneration of the original shape may be ascribable to disulfide bond scission in dark. The leuco form reduced the disulfide, restoring the skeletal carbonyl groups and regenerating the thiol groups.

In addition, the leuco form **4c** was chemically converted to **5c** (50% yield) by oxidation with chloranil. The analytical results for this compound, isolated by oxidation of the leuco form, were exactly the same as those of **5c** synthesised from **2c**.

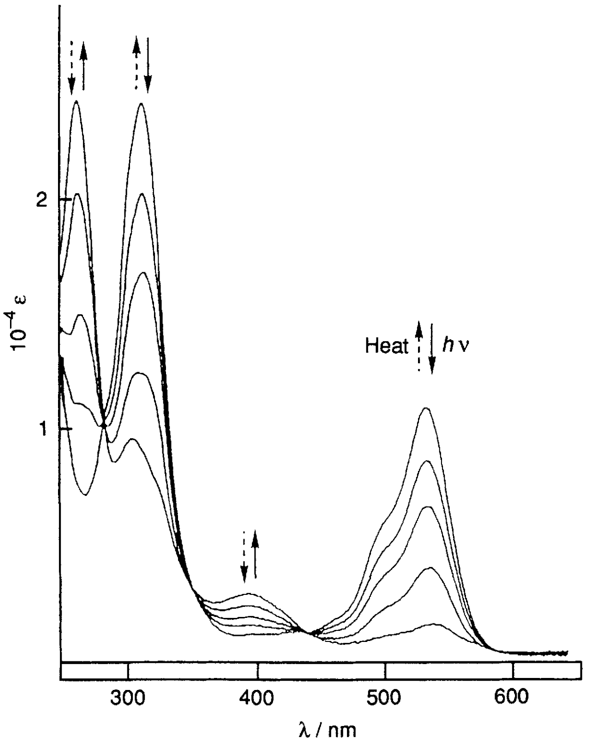
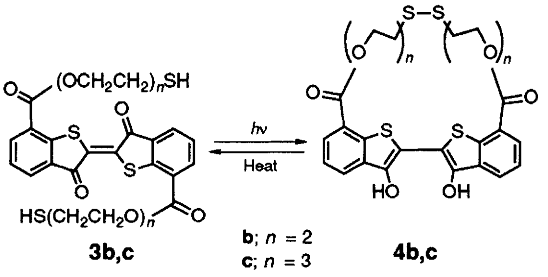


Fig. 1 Spectral changes on photolysis of 1.23×10^{-5} mol dm^{-3} **3c** and thermal reversion in 1,2-dichloroethane at $\lambda > 550$ nm



Scheme 2

From these results we conclude that upon irradiation the excited carbonyl groups easily abstract protons from the thiol groups followed by intramolecular disulfide formation; in the dark thermal scission of the disulfide bond by the hydroxy groups of the leuco form occurs. Compound **3b** behaved similarly, but, interestingly, compound **3a** showed *cis–trans* photoisomerization[5] instead of a photo-redox reaction, the λ_{max} for the *trans* and *cis* forms being 537 and 488 nm respectively. A Corey–Pauling–Koltun (CPK) model of **3a** shows that the two thiol groups remain so far from each other that a disulfide bond cannot be formed.

The thioindigo derivatives having a dithiol–disulfide couple reported herein are thus potentially important as a new type of photochromic compound.

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