Photochemical *cis–trans*-Isomerization of *trans*-Bis-2,2'-(3-oxo-2,3-dihydrobenzo[*b*]furylidine) (Oxindigo)

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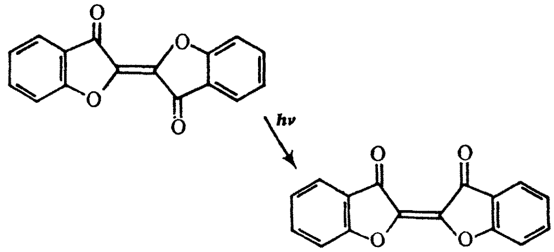
THERE is considerable interest in the geometrical isomerization of the indigo chromophore system.[1] Wyman and Brode[2] chromatographically separated the thermally unstable *cis*-bis-2,2'-(3-oxo-2,3-dihydrobenzo[*b*]thienylidene) (thioindigo) from an irradiated solution of the *trans*-isomer. Attempts to isolate *cis*-oxindigo have failed.[3] We now report the photochemical *cis–trans*-isomerization of oxindigo and the isolation of *cis*-oxindigo. U.v. irradiation‡ of the bright lemon yellow *trans*-oxindigo (100 mg.), m.p. 276—278°, in dry benzene (1600 ml.) under nitrogen for 3 hr.§ gave *cis*-oxindigo (16 mg.), m.p. 252—254°, after chromatography on cellulose in cyclohexane and crystallization from the same solvent. Most of the *cis*-oxindigo was extracted from the reaction mixture, before chromatography, by cyclohexane in which it alone is soluble.

The i.r. spectrum (KBr) of *trans*-oxindigo contains bands at 1692 (C=O) and 858 cm.$^{-1}$ whilst *cis*-oxindigo has bands at 1724 and 1681 cm.$^{-1}$ (C=O) as expected for a molecule with C_{2v}-symmetry; the latter compound also had absorption at 1647 (C=C) and 882 cm.$^{-1}$. The difference in the carbonyl absorption for the *trans*- and *cis*-isomers agrees with i.r. spectral studies on *trans*- and *cis*-thioindigo[1c] and on *trans*- and *cis*-dibenzoylethylene[5] as well as with PPP-calculations for the geometric and rotational isomers of the indigo dyes.[6] The u.v. spectrum of *trans*-oxindigo [λ_{max} (C_6H_{12}) 413 nm., (1·38 × 10^4)] shows a longer wavelength absorption than *cis*-oxindigo [λ_{max} 396 nm., (1·31 × 10^4)]. This spectral behaviour parallels that of other *cis*- and *trans*-indigo dyes[1–3] and is similar to that found for



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[‡] Medium-pressure mercury immersion arc lamp (Osram S 81).

[§] Prolonged irradiation causes a colour change from yellow to red.

the *cis*- and *trans*-isomers of aromatic substituted ethylenic compounds.[1a,7]

Irradiation with 405 nm. of the *trans*- or the *cis*-isomer in benzene gives an equilibrium mixture containing 59% of the *cis*-isomer. The quantum yield for the *trans* → *cis*-isomerization is 0·63 and for the *cis* → *trans*-isomerization, 0·35. As expected from this result, *trans*-oxindigo does not fluoresce at room temperature.

From MO-calculations on indigo dyes with different hetero-atoms[8] the π-electron density of the central C=C bond increases in the order of $N < S \leqslant Se < O$. In the same order the *cis*-indigo compounds becomes thermally more stable. A benzene solution of *cis*-oxindigo is not isomerized at room temperature during 4 weeks.¶ Attempts to isomerize *cis*-oxindigo at 100° in xylene with, and without, exclusion of oxygen resulted in a slow fading of the yellow colour due to decomposition. Mass spectra of both *trans*- and *cis*-oxindigo show that *cis*-oxindigo is much the less stable compound. The *trans*-form shows a simple mass spectrum (m/e 264 = 100% peak); the molecular peak intensity of *cis*-oxindigo is only 60% and a fragmentation with loss of 4 CO is indicated. The mass spectrum of *cis*-oxindigo shows no evidence of a carbene dissociation (no ion at m/e 132), as recently was observed in the mass spectrum of a similar compound.[9]

The author thanks Dr. D. Schulte-Frohlinde for his support of this work.

(*Received, November 7th*, 1968; *Com.* **1516**.)

¶ Thermal *cis–trans* isomerization of indigo dyes in solution at room temperature has been reported; *cis-NN*-dimethylindigo reverts to the *trans*-isomer in 30 sec., *cis*-thioindigo (ref. 2) in 32 hr., *cis*-selenoindigo (ref. 3) still slower.

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