

Synthesis of *N,N'*-Diacylindigotins (*N,N'*-Diacyl-2,2'-bi-indolinylidene-3,3'-diones) via an Oxidative Oxygen-to-Nitrogen Acyl Shift of *O,O'*-Diacyl-leucoindigos(3,3'-Diacyloxy-2,2'-bi-indolyls) †

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O,O'-Diacyl-leucoindigos (**3f–j**), which were readily obtained by the reaction of leucoindigo disodium salt (**4**) with acyl chlorides, underwent rapid oxidation by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to generate the indigo chromophore with concomitant shift of the acyl groups intramolecularly from oxygen to nitrogen. A number of *N,N'*-diacylindigotins with functionalized acyl groups were prepared by this method [(**2a**), (**2f–j**)] and the direct *N*-acylation method [(**2a–e**)]. A large bathochromic shift of the visible absorption band in the *cis* form of *N,N'*-diacylindigotins with bulky acyl groups (**2c**), (**2d**), and (**2j**) was observed which suggested that the electronic structure of the indigo chromophore is perturbed by the steric constraint of the *N*-acyl groups.

The photochemical properties of dyes have recently attracted much attention as a result of progress in the application of light-absorbing substances to a variety of photo devices.^{1,2} The indigo chromophore is regarded as one of the most intriguing photoresponsive systems known, undergoing as it does *trans-cis* photoisomerization^{3–6} and photo oxidoreduction⁷ upon irradiation at its visible absorption band; the latter is in the range 400–700 nm depending upon the substituents present. It was suggested that *N,N'*-diacylindigotin ‡ had potential as an energy-storing substance in view of the photochemical *trans* to *cis* isomerization and the reverse exothermic process.^{8,9} Despite the growing interest in indigotin derivatives, only a limited number of *N,N'*-diacylindigotins have been synthesized, the *N*-acylation being difficult because (i) of indigotin's sparing solubility in ordinary solvents, (ii) lowering of the reactivity of the indigotin nitrogen as a result of conjugation with the carbonyl group, and (iii) intramolecular hydrogen bonding. In view of these problems, this present work was undertaken with the objective of developing a general method for the *N,N'*-diacylation of indigotin.

Results and Discussion

Whereas the reaction of indigotin (**1**) with aromatic acyl chlorides in pyridine at reflux temperature generally affords fair yields of *N,N'*-diacylindigotins,¹⁰ *N*-acylation with aliphatic acyl chlorides was ineffective under similar reaction conditions. However, *N,N'*-diacetylindigotin (**2a**) is obtained in a good yield when (**1**) is treated with an excess of acetyl chloride in acetic anhydride;^{11,12} acetic anhydride however cannot be used as a solvent for the preparation of other *N,N'*-diacylindigotins. In our work we have prepared *N,N'*-dipropionyl- (**2b**), *N,N'*-diisobutyryl- (**2c**), *N,N'*-bis(cyclohexylcarbonyl)- (**2d**), and *N,N'*-

Table 1. Yields of the direct *N*-acylation (1)→(2)

Compound	R ^a	Temp. (°C)	Time (h)	Yield (%)
(2b)	Et	100	15	44
(2c)	Pr ⁱ	90	36	40
(2d)	<i>c</i> -C ₆ H ₁₁	120	5	31
(2e)	PhCH ₂ CH ₂	100	13	47
(2k)	Bu ⁱ	120	15	0
(2m)	3-Pyridyl	50	5	68
(2n)	<i>N</i> -Methyl-3-pyridinio	60	1	47 ^b

^a R denotes amide-carbonyl substituent of (**2**). ^b The data are for the reaction of (**2m**) with dimethyl sulphate.

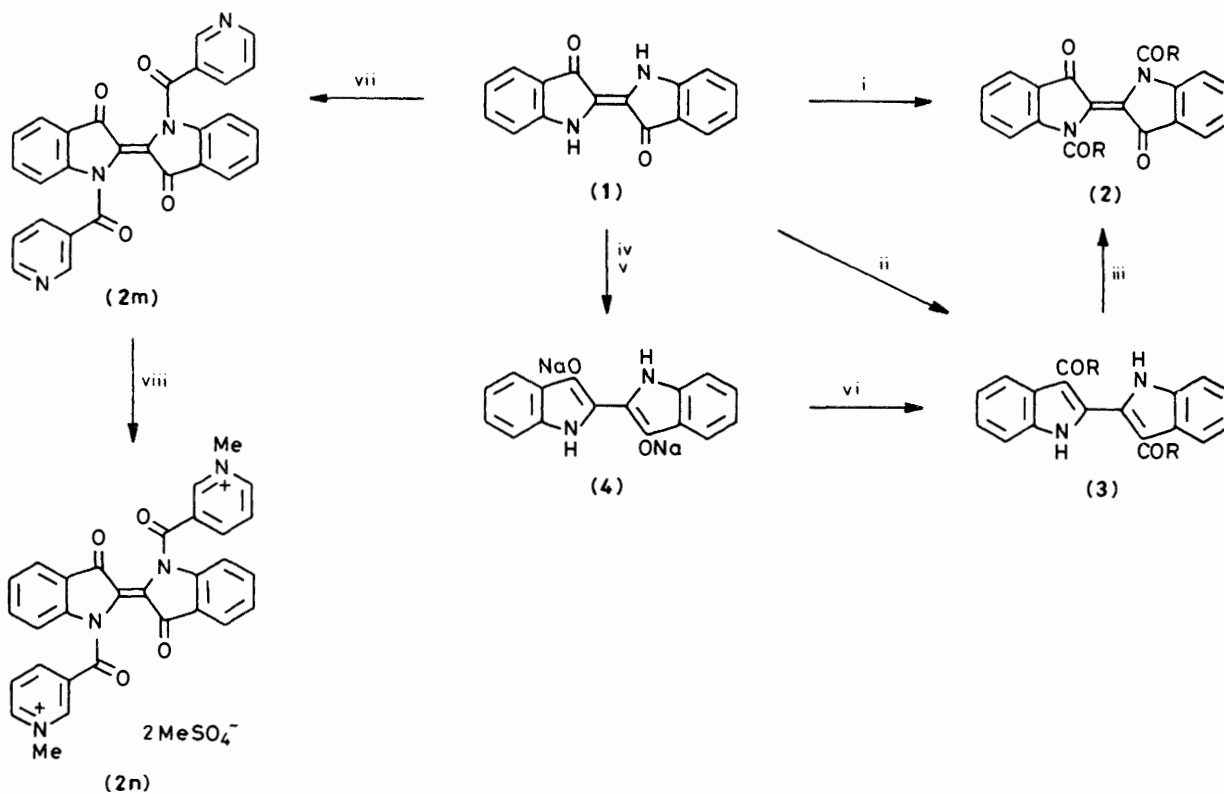
bis(3-phenylpropionyl)-indigotin (**2e**) by allowing (**1**) to react with the corresponding acyl chloride in *n*-butyl acetate using 2,6-dimethylpyridine as a HCl scavenger according to the reaction conditions shown in Table 1.

Although direct *N*-acylation can generally be used for simple aliphatic acid chlorides, in the above reactions, the relatively low yields of product (<50% as a result of partial decomposition of the products under the reaction conditions) and the fact that *N,N'*-diacylindigotins were not formed at all by direct *N*-acylation with acyl chlorides having a bulky acyl function or containing an active methylene functionality (e.g. pivaloyl chloride or phenylacetyl chloride) made the development of alternative acylation procedures desirable. Earlier it was noted that *O,O'*-diacetyl-leucoindigo † (**3a**) was oxidized to give *N,N'*-diacetylindigotin (**2a**) and *N*-acetyl-anthranilic acid on treatment with sodium nitrite, potassium permanganate, or chromium trioxide in acetic acid.^{13,14} The synthetic utility of this reaction was not, however, further explored.

When *O,O'*-diacetyl-leucoindigo (**3a**) was treated with a slight excess of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in acetone at room temperature, the solution rapidly turned red indicating the ready formation of *N,N'*-diacetylindigotin (**2a**)—the reaction was monitored photospectroscopically. A 92% yield of (**2a**) was obtained upon work-up. *O,O'*-Bis(ethoxycarbonyl)leucoindigo (**3f**) was prepared in 47% yield by an anal-

† This paper includes the detail for part of the work described in the preliminary communication *J. Chem. Soc., Chem. Commun.*, 1982, 1022.

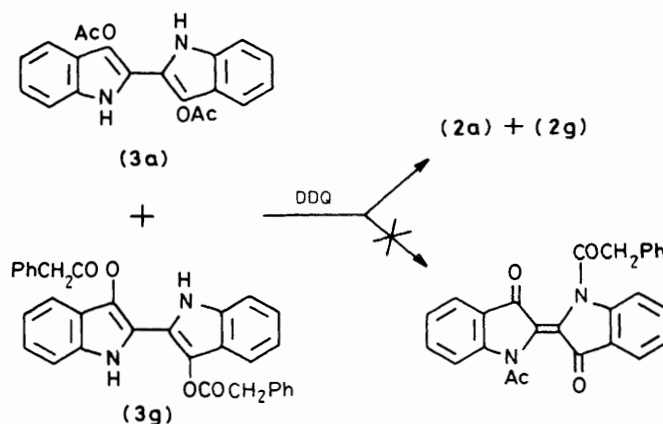
‡ For convenience the names indigotin and leucoindigo have been used in the Discussion part of the paper, whilst the compounds have been named systematically (as bi-indolinylidenes and bi-indolyls) in the Experimental section.



Scheme 1. Reagents: i, RCOCl, 2,6-dimethylpyridine, n-butyl acetate, for (2b–e); ii, Zn, RCOCl, NaOAc, AcOEt, for (3a, f); iii, DDQ, DMSO, for (2a, f–j); iv, Zn, EtOH; v, NaH, THF; vi, RCOCl, for (3g–l); vii, nicotinoyl chloride hydrochloride, pyridine; viii, Me₂SO₄

ogous procedure to (3a), that is, (1) was reduced with zinc dust in the presence of ethoxycarbonylacetyl chloride and sodium acetate. Oxidation of (3f) with DDQ in dimethyl sulphoxide (DMSO) occurred smoothly to give *N,N'*-bis(ethoxycarbonylacetyl)indigotin (2f) which, although reasonably stable in benzene solution, decomposed on silica gel, in methanol solution, and upon irradiation ($\lambda > 500$ nm) in chloroform solution. Since *O,O'*- α -arylacetyl-leucoindigo (3g–j) and *O,O'*-*t*-alkylcarbonyl-leucoindigo (3k, l) could not be obtained from (1) by the one-step procedure described above, (1) was first reduced by zinc dust to leucoindigo; the latter was then converted into the disodium salt (4) and allowed to react with the corresponding acyl chloride to afford (3g–l) in ca. 80% yield (see Scheme 1). The oxidative oxygen-to-nitrogen shift of the acyl group took place to afford *N,N'*-bis(phenylacetyl)- (2g), *N,N'*-bis(*p*-methoxyphenylacetyl)- (2h), *N,N'*-bis(1-naphthylacetyl)- (2i), and *N,N'*-bis(2-phenylbutyryl)-indigotin (2j) as summarized in Table 2. The yields of the *N,N'*-diacylindigotin obtained by the oxidative O-to-N acyl shift decreased with increasing bulkiness of the acyl group so that for the pivaloyl and 1-adamantyl-carbonyl substituted compounds there was no shift. This indicated the limitation originating from the steric constraints between the N-substituents and the peri-position of the indigo nucleus in the formation of *N,N'*-disubstituted indigotin.

Oxidizing agents weaker than DDQ (chloranil and *o*-chloranil) failed to induce the acyl shift reaction which is considered to be initiated by the oxidation of the leucoindigo π -electron system. Monitoring of the visible spectrum showed a rapid growth of the absorption band at 390 nm during the early stage of the reaction of *O,O'*-diacetyl-leucoindigo (3a) with DDQ. A similar spectral change was also observed just after DDQ was added to *O,O'*-dipivaloyl-leucoindigo (3k) and the ¹H n.m.r. spectrum of this reaction mixture in (CD₃)₂SO showed two new singlets at δ 1.11 and 1.43 besides the original singlet at δ 1.28



Scheme 2.

due to the *t*-butyl group of (3k). These observations support the initial formation, in an equilibrium mixture, of a charge-transfer complex between DDQ and *O,O'*-diacyl-leucoindigo; the charge-transfer complex can collapse to *N,N'*-diacyl-indigotin and DDQH₂ unless the acyl group is quite bulky. Evidence in support of the intramolecular acyl shift from oxygen to nitrogen was provided by the absence of the crossed product, *N*-acetyl-*N'*-phenylacetylindigotin, when a mixture of (3a) and (3g) was treated with DDQ (Scheme 2).

The synthesis of water-soluble *N,N'*-diacylindigotins was attempted in order to study the photochemical properties of *N,N'*-diacylindigotin derivatives in aqueous solution. Since the *N*-acylation of Indigo Carmine (sodium indigotin sulphate) was unsuccessful because of solubility problems, *N,N'*-dinicotinoyl-indigotin (2m), prepared according to an established

procedure,¹⁰ was treated with an excess of dimethyl sulphate to afford the *N*-methylpyridinium salt (**2n**). Compound (**2n**) which is hygroscopic and soluble in water and methanol undergoes hydrolysis at its linkage as a result of the electron-withdrawing effect of the *N*-methylpyridinium moiety on the amide bond.

Since *N,N'*-diacylindigotin exists in both *trans* and *cis* forms, spectral data for both were determined according to the method of Blanc and Ross¹¹ (see Table 3). The chromophore of indigotin is regarded as a donor-acceptor type in which the position of the absorption band depends on the electron density on the nitrogen.^{15,16} The absorption spectra of (**2a–d**) in their *trans* forms show a consecutive red shift with increasing number of alkyl substituents on the acyl α -carbon; the absorption band of (**2f**) which has an electron-withdrawing substituent on the acyl α -carbon is blue shifted compared with that of (**2a**). This trend in spectral changes with acyl groups is rationalized in terms of the electronic effect of the substituent at the acyl α -carbon through σ bonds on the electron density of the nitrogen. The absorption maxima of the *cis* *N,N'*-diacylindigotins with bulky acyl groups (**2c**), (**2d**), and (**2j**) are 30–40 nm longer in

wavelength than that of *cis*-(**2a**). This red shift is explainable mainly on the basis of the steric constraint of the two acyl groups in the *cis* form which would twist the central C–C bond, destabilize the ground state, and relieve the electrostatic repulsion between the two carbonyl oxygens of the indigo nucleus to a greater extent in the excited state than in the ground state. The excited state of the indigo chromophore is pictured as having a central C–C single bond and charged oxygen and nitrogen atoms.

Experimental

¹H N.m.r. spectra were taken on Hitachi R-24 (60 MHz) and JEOL MH-100 (100 MHz) instruments using tetramethylsilane as an internal standard. I.r. spectra were recorded for KBr discs on a Shimadzu IR-420 machine and visible spectra were recorded on a Shimadzu UV-240 instrument. Wakogel C-300 was used for silica gel column chromatography.

General Procedure for the Direct N-Acylation of 2,2'-Bi-indolinylidene-3,3'-dione (Indigotin).—A mixture of 2,2'-bi-indolinylidene-3,3'-dione (2.62 g), acyl chloride (5 ml), 2,6-dimethylpyridine (5 ml), and *n*-butyl acetate (50 ml) was heated at 90–120 °C for 5–36 h (see Table 1). The solvent and excess of acyl chloride were removed under reduced pressure and the residue was dissolved in benzene; the insoluble 2,6-dimethylpyridine hydrochloride was then filtered off. The benzene filtrate was evaporated and purified by chromatography on silica gel with benzene as eluant.

N,N'-Dipropionyl-2,2'-bi-indolinylidene-3,3'-dione (**2b**). The product was recrystallized from chloroform-methanol, ν_{\max} . 1705, 1680, and 1595 cm⁻¹; δ (CDCl₃) 8.3–7.1 (8 H, m, 8 × ArH), 2.85 (4 H, q, 2 × COCH₂), 1.29 (6 H, t, 2 Me).

N,N'-Di-isobutyryl-2,2'-bi-indolinylidene-3,3'-dione (**2c**). The

Table 2. Yields of the oxidative O-to-N acyl shift (3)→(2)

Compound	R ^a	Yield (%)
(2a)	Me	92 ^b
(2f)	EtOCOCH ₂	83
(2g)	PhCH ₂	70
(2h)	<i>p</i> -MeOC ₆ H ₄ CH ₂	68
(2i)	C ₁₀ H ₇ CH ₂	60
(2j)	Et(Ph)CH	55
(2k)	Bu ¹	0
(2l)	1-Adamantyl	0

^a R denotes amide-carbonyl substituent of (2). ^b In acetone instead of DMSO for the rest.

Table 3. Analytical and spectral data for the *N,N'*-diacylindigotins

Compound (Formula)	M.p. (°C) (decomp.)	Found (%) (Required)				Visible spectra (in C ₆ H ₆)		
		C	H	N		λ_{\max} (nm)	$\epsilon(\lambda_{\max}^{cis})$	$\epsilon(\lambda_{\max}^{trans})$
(2a) (C ₂₀ H ₁₄ N ₂ O ₄)	256–257	—	—	—	<i>cis</i>	438	4460	510
(2b) (C ₂₂ H ₁₈ N ₂ O ₄)	206–207	70.85 (70.58)	4.55 (4.85)	7.55 (7.48)	<i>trans</i> <i>cis</i>	562 440	600 4340	7020 810
(2c) (C ₂₄ H ₂₂ N ₂ O ₄)	221–223	71.9 (71.63)	5.46 (5.51)	6.91 (6.96)	<i>cis</i> <i>trans</i>	477 576	3810 600	550 6950
(2d) (C ₃₀ H ₃₀ N ₂ O ₄)	231–232	74.65 (74.67)	6.2 (6.27)	5.55 (5.80)	<i>cis</i> <i>trans</i>	476 579	4080 560	440 7530
(2e) (C ₃₄ H ₂₆ N ₂ O ₄)	190–192	77.41 (77.55)	4.85 (4.94)	5.05 (5.32)	<i>cis</i> <i>trans</i>	435 565	4100 560	560 6980
(2f) (C ₂₆ H ₂₂ N ₂ O ₈)	(ca. 80)	64.1 (63.67)	4.5 (4.52)	5.6 (5.71)	<i>cis</i> <i>trans</i>	424 552	3970 980	780 6420
(2g) (C ₃₂ H ₂₂ N ₂ O ₄)	163–165	77.05 (77.09)	4.05 (4.45)	5.4 (5.62)	<i>cis</i> <i>trans</i>	439 568	4200 560	420 7160
(2h) (C ₃₄ H ₂₆ N ₂ O ₆)	158–160	73.25 (73.11)	4.55 (4.69)	5.1 (5.02)	<i>cis</i> <i>trans</i>	430 570	4200 1200	180 7170
(2i) (C ₄₀ H ₂₆ N ₂ O ₄)	187–189	79.85 (80.25)	3.9 (4.38)	4.45 (4.68)	<i>cis</i> <i>trans</i>	431 566	4630 1180	360 6590
(2j) (C ₃₆ H ₃₀ N ₂ O ₄)	174–176	78.2 (77.96)	5.25 (5.45)	5.25 (5.05)	<i>cis</i> <i>trans</i>	464 578	3560 600	320 7130
(2m) (C ₂₈ H ₁₆ N ₄ O ₄)	243–245	70.9 (71.18)	3.55 (3.41)	11.65 (11.86)	<i>trans</i>	569	—	3980
(2n) (C ₃₂ H ₂₈ N ₄ O ₁₂ S ₂)	—	—	—	—	<i>trans</i>	548 ^a	—	4920

^a Measured in acetonitrile.

product was recrystallized from benzene–n-hexane, ν_{\max} 1 705, 1 670, and 1 595 cm^{-1} ; $\delta(\text{CDCl}_3)$ 8.3–7.2 (8 H, m, $8 \times \text{ArH}$), 3.36 (2 H, sep, $2 \times \text{COCH}$), 1.24 (12 H, d, 4 Me).

N,N'-Bis(cyclohexylcarbonyl)-2,2'-bi-indolinylidene-3,3'-dione (**2d**). Since the product decomposed on silica gel, it was purified only by recrystallization from chloroform–ethanol, ν_{\max} 1 705, 1 670, and 1 595 cm^{-1} ; $\delta(\text{CDCl}_3)$ 8.1–7.1 (8 H, m, $8 \times \text{ArH}$), 2.99 (2 H, m, $2 \times \text{COCH}$), and 2.3–1.0 (20 H, m, $10 \times \text{CH}_2$).

N,N'-Bis(3-phenylpropionyl)-2,2'-bi-indolinylidene-3,3'-dione (**2e**). The product was recrystallized from benzene–n-hexane, ν_{\max} 1 705, 1 675, and 1 600 cm^{-1} ; $\delta(\text{CDCl}_3)$ 8.1–6.8 (18 H, m, $18 \times \text{ArH}$) and 2.98 (8 H, s, $2 \times \text{COCH}_2\text{CH}_2$).

3,3'-Bis(ethoxycarbonylacetoxyl)-2,2'-bi-indolyl (**3f**).—A mixture of 2,2'-bi-indolinylidene-3,3'-dione (2.62 g), ethoxycarbonylacetate chloride (14 ml), zinc dust (7.5 g), sodium acetate (2.05 g), and ethyl acetate (100 ml) was stirred at room temperature for 30 min and then at 40 °C for 2 h. After ethyl acetate had been removed under reduced pressure, the residue was extracted into hot acetone. The acetone filtrate was evaporated and methanol was added to give a yellow precipitate of (**3f**) (47%, 2.31 g), ν_{\max} 3 300, 1 760, and 1 710 cm^{-1} ; $\delta[(\text{CD}_3)_2\text{SO}]$ 11.16 (2 H, s, $2 \times \text{NH}$), 7.8–7.1 (8 H, m, $8 \times \text{ArH}$), 4.37 (4 H, q, $2 \times \text{OCH}_2$), 3.95 (4 H, s, $2 \times \text{COCH}_2\text{CO}_2$), 1.34 (6 H, t, $2 \times \text{Me}$) (Found: C, 62.95; H, 4.9; N, 5.3. Calc. for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_8$: C, 63.41; H, 4.88; N, 5.69%).

General Procedure for the Preparation of 3,3'-Diacloxy-2,2'-bi-indolyl.—2,2'-Bi-indolinylidene-3,3'-dione (2.62 g) was reduced to 2,2'-bi-indolyl-3,3'-diol by treatment with zinc dust (5 g) at 80 °C for 2 h in 95% ethanol (100 ml) pre-treated with SO_2 gas. After the solvent had been removed under reduced pressure, dry tetrahydrofuran (150 ml) and 50% sodium hydride in mineral oil (0.96 g) were added under a nitrogen stream at 0 °C to give an orange suspension. The mixture was stirred for 30 min, after which acyl chloride (25 mmol) in THF (50 ml) was added dropwise; the resulting mixture was then stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in DMSO, the excess of zinc dust being filtered off. The DMSO filtrate was poured into water and the precipitate of 3,3'-diacloxy-2,2'-bi-indolyl so formed was collected, washed with methanol, and dried *in vacuo*; the yields of product were ca. 80%. The spectral properties of (**3g**–**l**) are as follows.

3,3'-Bis(phenylacetoxyl)-2,2'-bi-indolyl (**3g**): ν_{\max} 3 410 and 1 740 cm^{-1} ; $\delta[(\text{CD}_3)_2\text{SO}]$ 11.53 (2 H, s, $2 \times \text{NH}$), 7.7–6.8 (18 H, m, $18 \times \text{ArH}$), and 4.05 (4 H, s, $2 \times \text{COCH}_2$).

3,3'-Bis(*p*-methoxyphenylacetoxyl)-2,2'-bi-indolyl (**3h**): ν_{\max} 3 350 and 1 730 cm^{-1} ; $\delta[(\text{CD}_3)_2\text{SO}]$ 11.42 (2 H, s, $2 \times \text{NH}$), 7.5–6.8 (16 H, m, $16 \times \text{ArH}$), 3.92 (4 H, s, $2 \times \text{COCH}_2$), and 3.62 (6 H, s, $2 \times \text{OMe}$).

3,3'-Bis(1-naphthylacetoxyl)-2,2'-bi-indolyl (**3i**): ν_{\max} 3 400 and 1 740 cm^{-1} ; $\delta[(\text{CD}_3)_2\text{SO}]$ 11.41 (2 H, s, $2 \times \text{NH}$), 8.3–6.9 (22 H, m, $22 \times \text{ArH}$), and 4.52 (4 H, s, $2 \times \text{COCH}_2$).

3,3'-Bis(2-phenylbutyryloxy)-2,2'-bi-indolyl (**3j**): ν_{\max} 3 435 and 1 760 cm^{-1} ; $\delta[(\text{CD}_3)_2\text{SO}]$ 11.28 (s, 2 H, $2 \times \text{NH}$), 7.5–6.7 (18 H, m, $18 \times \text{ArH}$), 4.30 (2 H, t, $2 \times \text{COCH}$), 1.94 (4 H, m, $2 \times \text{CH}_2$), and 0.88 (6 H, t, $2 \times \text{Me}$).

3,3'-Bis(pivaloyloxy)-2,2'-bi-indolyl (**3k**): ν_{\max} 3 420 and 1 740 cm^{-1} ; $\delta[(\text{CD}_3)_2\text{SO}]$ 11.05 (2 H, s, $2 \times \text{NH}$), 7.3–6.8 (8 H, m, $8 \times \text{ArH}$), and 1.28 (18 H, s, $6 \times \text{Me}$).

3,3'-Bis(1-adamantylcarbonyloxy)-2,2'-bi-indolyl (**3l**): ν_{\max} 3 450 and 1 745 cm^{-1} ; $\delta[(\text{CD}_3)_2\text{SO}]$ 10.72 (2 H, s, $2 \times \text{NH}$), 7.1–6.8 (8 H, m, $8 \times \text{ArH}$), 2.1–1.5 (30 H, m, $12 \times \text{CH}_2$ and $6 \times \text{CH}$).

General Procedure for the Preparation of N,N'-Diacyl-2,2'-bi-indolinylidene-3,3'-diones via an Oxidative O-to-N Acyl Shift.—DDQ (1.2 mol equiv.) was added to a DMSO solution (10 ml) of 3,3'-diacloxy-2,2'-bi-indolyl (1 g). The mixture was stirred for 1 h at room temperature and then poured into water. The precipitate so formed was filtered off, washed with water, dried *in vacuo*, and then dissolved in benzene, the DDQH_2 being filtered off. The product was then purified by column chromatography on silica gel with benzene as eluant.

N,N'-Bis(ethoxycarbonylacetate)-2,2'-bi-indolinylidene-3,3'-dione (**2f**). Since this compound decomposed on silica gel, cellulose powder (Whatman CF-11) was used for the column chromatography with benzene as eluant; ν_{\max} 1 700, 1 675, and 1 595 cm^{-1} ; $\delta(\text{CDCl}_3)$ 8.4–7.3 (8 H, m, $8 \times \text{ArH}$), 4.10 (4 H, q, $2 \times \text{OCH}_2$), 4.0 (4 H, bs, $2 \times \text{COCH}_2\text{CO}_2$), and 1.07 (6 H, t, $2 \times \text{Me}$).

N,N'-Bis(phenylacetate)-2,2'-bi-indolinylidene-3,3'-dione (**2g**). This was recrystallized from benzene–ethanol, ν_{\max} 1 710, 1 675, and 1 600 cm^{-1} ; $\delta(\text{CDCl}_3)$ 8.3–7.1 (18 H, m, $18 \times \text{ArH}$) and 4.12 (4 H, s, $2 \times \text{COCH}_2$).

N,N'-Bis(*p*-methoxyphenylacetate)-2,2'-bi-indolinylidene-3,3'-dione (**2h**). This was recrystallized from benzene–ethanol, ν_{\max} 1 710, 1 670, and 1 600 cm^{-1} ; $\delta(\text{CDCl}_3)$ 8.1–6.5 (16 H, m, $16 \times \text{ArH}$), 4.00 (4 H, s, $2 \times \text{COCH}_2$), and 3.62 (6 H, s, $2 \times \text{OMe}$).

N,N'-Bis(1-naphthylacetate)-2,2'-bi-indolinylidene-3,3'-dione (**2i**). This was recrystallized from chloroform–ethanol, ν_{\max} 1 705, 1 680, and 1 600 cm^{-1} ; $\delta(\text{CDCl}_3)$ 8.1–6.6 (22 H, m, $22 \times \text{ArH}$) and 4.40 (4 H, s, $2 \times \text{COCH}_2$).

N,N'-Bis(2-phenylbutyryl)-2,2'-bi-indolinylidene-3,3'-dione (**2j**). This was recrystallized from ethanol, ν_{\max} 1 715, 1 680, and 1 600 cm^{-1} ; $\delta(\text{CDCl}_3)$ 8.1–6.7 (18 H, m, $18 \times \text{ArH}$), 4.23–3.96 (2 H, m, $2 \times \text{COCH}$), 2.7–1.8 (4 H, m, $2 \times \text{CH}_2$), and 0.99–0.72 (6 H, m, $2 \times \text{Me}$).

N,N'-Dinicotinoyl-2,2'-bi-indolinylidene-3,3'-dione (**2m**) and its *N,N'*-dimethylpyridinium bis(methyl sulphate) salt (**2n**). A mixture of 2,2'-bi-indolinylidene-3,3'-dione (3.93 g) and nicotinoyl chloride hydrochloride (13.3 g) in pyridine (50 ml) was heated at 50 °C for 5 h. The reaction mixture was poured into water and the resulting precipitate was filtered off and dissolved in chloroform. The solution was then dried (Na_2SO_4), and evaporated, and the residue chromatographed on silica gel with benzene–acetone as eluant to give *N,N'*-dinicotinoyl-2,2'-bi-indolinylidene-3,3'-dione (**2m**) (68%, 4.66 g), ν_{\max} 1 680 and 1 610 cm^{-1} ; $\delta(\text{CDCl}_3)$ 9.28 (2 H, d, $2 \times \text{py-}\alpha\text{-H}$), 8.95 (2 H, dd, $2 \times \text{py-}\alpha\text{-H}$), 8.38 (2 H, dt, $2 \times \text{py-}\gamma\text{-H}$), and 8.0–7.2 (10 H, $8 \times \text{ArH}$ and $2 \times \text{py-}\beta\text{-H}$).

When compound (**2m**) (500 mg) was treated with dimethyl sulphate (5 ml) at 60 °C for 1 h, a clear red solution was obtained. Dilution of this with diethyl ether afforded a fine precipitate of (**2n**) (47%, 363 mg). Compound (**2n**) was filtered off under a stream of dry nitrogen and then recrystallized from acetonitrile–ethanol, $\delta(\text{CDCl}_3)$ 9.56 (2 H, s, $2 \times \text{py-}\alpha\text{-H}$), 9.11 (4 H, d, $2 \times \text{py-}\alpha\text{-H}$ and $2 \times \text{py-}\gamma\text{-H}$), 8.43 (2 H, dd, $2 \times \text{py-}\beta\text{-H}$), 8.0–7.4 (8 H, m, $8 \times \text{ArH}$), 4.51 (6 H, s, $2 \times \text{NMe}^+$), and 3.52 (6 H, s, $2 \times \text{MeSO}_4^-$).

Spectral Measurement of cis and trans Isomers of N,N'-Diacyl-2,2'-bi-indolinylidene-3,3'-diones (2a–j).—Visible absorption spectra were measured after benzene solutions of *N,N'*-diacyl-2,2'-bi-indolinylidene-3,3'-diones had been allowed to stand in the dark for several days (solutions assumed to contain 100% of their *trans* isomers¹⁷). Spectral data of the *cis* isomers were determined on the basis of the calculated *cis*–*trans* ratios of the benzene solutions of *N,N'*-diacyl-2,2'-bi-indolinylidene-3,3'-diones which were irradiated with visible light ($\lambda > 500 \text{ nm}$) using a high-pressure mercury lamp and an 0.1M-aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ as a filter. The *cis*–*trans* ratio was calculated

from the fluorescence intensity at 650 nm with the excitation at 365 nm according to the literature of Blanc and Ross.¹¹

References

- 1 J. Rochlitz, *Chimia*, 1980, **34**, 131.
- 2 H. Meier, *Top. Curr. Chem.*, 1976, **61**, 85.
- 3 Y. Omote, S. Imada, R. Terasaki, K. Fujiki, T. Nishio, and C. Kashima, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3397.
- 4 G. M. Wyman and A. F. Zenhäusern, *J. Org. Chem.*, 1965, **30**, 2348.
- 5 W. R. Brode, E. G. Pearson, and G. M. Wyman, *J. Am. Chem. Soc.*, 1954, **76**, 1034.
- 6 C. P. Klages, K. Kobs, and R. Memming, *Ber. Bunsenges. Phys. Chem.*, 1982, **86**, 716.
- 7 K. S. Schanze, C. Giannotti, and D. G. Whitten, *J. Am. Chem. Soc.*, 1983, **105**, 6326.
- 8 H. D. Scharf, J. Fleischhauer, H. Leismann, I. Ressler, W. Schleker, and R. Weitz, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 652.
- 9 Battelle Development Corporation, U.S.P., 4 004 572 (1977).
- 10 T. Posner, *Ber.*, 1926, **59**, 1977.
- 11 J. Blanc and D. L. Ross, *J. Phys. Chem.*, 1968, **72**, 2818.
- 12 C. Lieberman and F. Dickhuth, *Ber.*, 1891, **24**, 4130.
- 13 D. Vorländer and J. von Pfeiffer, *Ber.*, 1919, **52**, 328.
- 14 W. Madelung, *Ber.*, 1924, **57**, 247.
- 15 P. W. Sadler, *J. Org. Chem.*, 1956, **21**, 316.
- 16 D. A. Rogers, J. D. Margerum, and G. M. Wyman, *J. Am. Chem. Soc.*, 1957, **79**, 2464.
- 17 W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Am. Chem. Soc.*, 1952, **74**, 4641.

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