

Inter- and intra-molecular selectivity in the cyclisation of *N*-cinnamoyl-1-naphthamides in solid-state photochemistry and *peri* selectivity in their photocyclisation in solution

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The photocyclisation of *N*-cinnamoyl-1-naphthamides **1a–f** was examined in the solid state and in solution. Three types of cyclisation, intramolecular $2\pi + 2\pi$ and $4\pi + 2\pi$, and intermolecular $2\pi + 2\pi$ cyclisations were observed in the solid state. The ratios of these products were largely dependent on the substituents at the *para*-position of the cinnamoyl moiety. Single-crystal X-ray crystallographic analysis of **1b** showed that the intermolecular distance between the two double bonds was 4.34 Å. Amides with bulky substituents preferred intramolecular $2\pi + 2\pi$ cyclisation. In contrast to the solid-state photochemistry, only intramolecular cyclisation was observed in solution. The ratios of $2\pi + 2\pi$ and $4\pi + 2\pi$ cyclisation products were irradiation time dependent. It was found that the $2\pi + 2\pi$ cycloreversion and rearrangement from the $2\pi + 2\pi$ product to the *endo* $4\pi + 2\pi$ isomer were the cause of this dependency.

Molecules possessing two reactive sites (**A** and **B**) may undergo either intramolecular (**A–B**) or intermolecular (**A–A**, **A–B** and **B–B**) reactions, or a combination of the two. The control of these reactions should be fundamental in synthetic organic chemistry. One option for controlling inter- or intra-molecular selectivity is the use of solid state photochemistry.¹ As exemplified by many elegant works, it has the advantage over photochemistry in solution in stereoselectivity² and intermolecular cyclisation³ is especially favoured due to the packing arrangement of molecules in the crystalline environment. To investigate the factors which control this inter-/intra-molecular reactivity in photochemistry, the solid-state photocyclisation of the naphthamide derivatives **1** was carried out and the results were compared with their photocyclisation in solution. The amide **1** possesses two reactive sites for cyclisation, the naphthoyl (**A**) and acryl (**B**) moieties. Intramolecular cyclisation **A–B** represents either $2\pi + 2\pi$ or $4\pi + 2\pi$ cyclisation between **A** and **B** moieties, and intermolecular **A–A**, **A–B** and **B–B** cyclisations refer to $4\pi + 4\pi$, $2\pi + 2\pi$ or $4\pi + 2\pi$, and $2\pi + 2\pi$ cyclisations between the corresponding reactive sites in an intermolecular way, respectively.

As a reference experiment, photocyclisation of **1a–h** in solution was carried out using benzene as a solvent and irradiation by high-pressure mercury lamp through a Pyrex glass filter (Scheme 1). It resulted in the exclusive formation of intramolecular cyclisation products *via* $2\pi + 2\pi$ and $4\pi + 2\pi$ cyclisations, typical photocyclisations of naphthalene derivatives. The results are shown in Table 1. It is quite uncommon that both $2\pi + 2\pi$ ⁴ and $4\pi + 2\pi$ ⁵ cyclisations proceed together in the same molecule in naphthalene derivatives.⁶ The ratio of $2\pi + 2\pi$ and $4\pi + 2\pi$ cyclisation products is irradiation time dependent. In the early stage of the reaction, the $2\pi + 2\pi$ cyclisation product **2** predominated. The stereochemistry of **2a–2e** was determined to be *anti* from their NOE difference spectra, which showed a positive NOE enhancement for the phenyl protons when the proton **H_c** was irradiated. The *trans* olefin geometry of the amides was preserved in the products. With longer irradiation times, the amounts of the diastereoisomeric $4\pi + 2\pi$ cyclisation products **3** and **4** increased in inverse proportion to **2**. These two isomers were obtained as a

Table 1 Yields (%) of cyclisation products in solution^a

	R ¹	R ²	Time/h	2	3 + 4 (3:4)	1^b
1a	H	H	1	73	27 (68:32)	0
1b	Me	H	1	68	25 (74:26)	0
			4	16	80 (88:12)	0
1c	Cl	H	1	64	28 (62:38)	0
1d	MeO	H	1	77	22 (47:53)	0
1e	Bu ^t	H	1	64	22 (67:33)	0
			6	16	76 (80:20)	0
1f	H	Ph	1	28	0	54
			7	56	0	25

^a Yields after HPLC purification. ^b Recovery of **1**.

chromatographically inseparable mixture. Only some of the major isomers, **3a**, **3c** and **3d**, were separated in pure form by HPLC (column: Merck NH₂; 10 mm × 250 mm). The stereochemistry of these isomers was determined to be *endo* based on the positive NOE enhancement in their NOE difference spectra. The stereochemistry of the minor diastereoisomer **4** (*exo*) was deduced from their NOE difference spectra obtained as a mixture with **3**. Comparison of their chemical shifts showed characteristic features. In the *endo* isomer **3**, the proton **H_a** appeared at a lower field than that of *exo* isomer **4**. On the other hand, the proton **H_b** appeared at a higher field for **3**. The benzylic protons also gave characteristic resonances, appearing as a singlet in **3** and two sets of doublets in **4**. The cyclisation products showed characteristic coupling constants for protons **H_a** and **H_b**, so that J_{H_a, H_b} for the $2\pi + 2\pi$ adducts were 8.9–9.4 Hz and 1.4–1.6 Hz for the $4\pi + 2\pi$ adducts. The NOE data and the chemical shifts of **H_a** and **H_b** of **2**, **3** and **4** are summarized in Table 2.

In order to survey the $2\pi + 2\pi$ cycloreversion and the origin of the $4\pi + 2\pi$ cyclisation products, irradiation of **2a** was examined. The $2\pi + 2\pi$ cycloreversion of cyclobutanes to olefins occurs almost exclusively on heating,⁷ but can be performed under electron-transfer sensitized photochemical conditions.⁸ Fig. 1 shows the progress of the reaction (irradiated through Pyrex glass) monitored by ¹H NMR

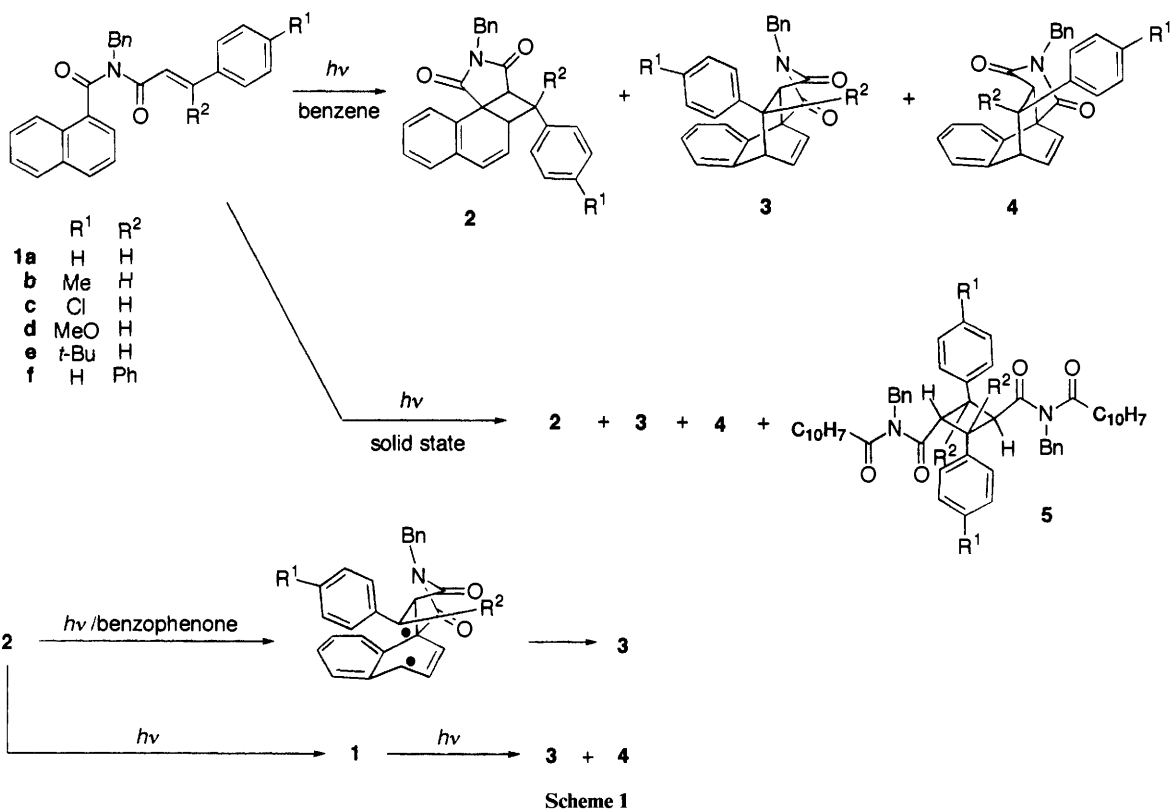
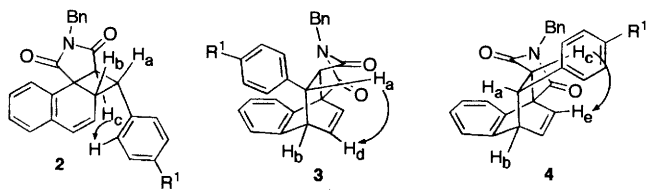


Table 2 NOE enhancement and chemical shifts of H_a and H_b of cyclisation products (in $CDCl_3$)

	NOE (%) H_c-H_{Ph}	NOE (%) H_a-H_d	NOE (%) H_c-H_e	δ_{H_a}	δ_{H_b}
2a	12.7			3.86	3.78
2b	12.2			3.93	3.87
2c	10.7			3.92	3.87
2d	11.9			3.91	3.86
2e	12.5			3.92	3.88
3a		2.5		3.42	4.05
3b		2.2		3.39	4.01
3c		2.6		3.39	4.00
3d		2.5		3.37	3.98
3e		2.1		3.39	4.04
4a			2.4	3.21	4.19
4b			3.3	3.20	4.20
4c			—	3.20	4.19
4d			2.7	3.19	4.18
4e			—	3.22	4.22



spectroscopy. The formation of **4a** reveals that this $4\pi + 2\pi$ cyclisation product may not be the secondary product derived directly from the rearrangement of **2a** since its formation requires two bond scissions in the cyclobutane ring. Instead, it might originate from **1a** which was formed *via* the $2\pi + 2\pi$ cycloreversion of **2a**. However, both routes would be possible for the formation of the other diastereoisomer **3a**. These two routes, the $2\pi + 2\pi$ cycloreversion and the direct rearrangement, were photosensitized by benzophenone. Control experiments showed that **2a** was inert under irradiation from a high-pressure mercury lamp through glass filters ($340 \text{ nm} < \lambda < 380 \text{ nm}$). Fig. 2 shows the progress of the

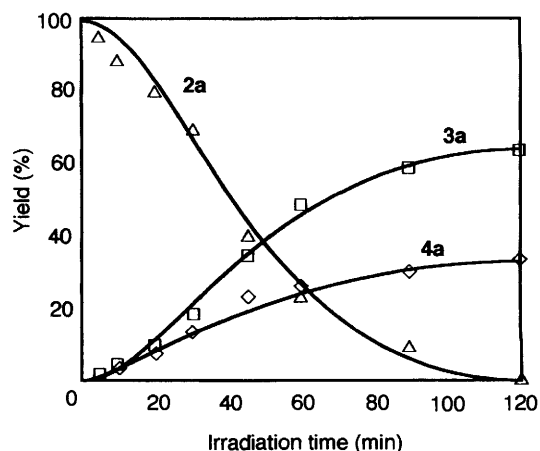


Fig. 1 Progress of the photorearrangement of **2a** ($5.1 \times 10^{-2} \text{ mol dm}^{-3}$) in C_6D_6 monitored by 1H NMR spectroscopy and irradiated by a high-pressure mercury lamp through a Pyrex filter ($\lambda > 280 \text{ nm}$)

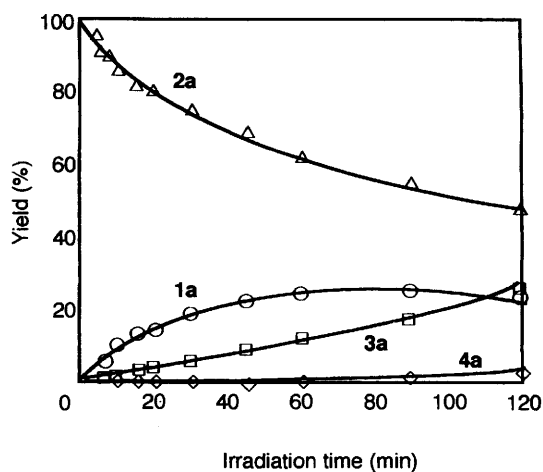


Fig. 2 Progress of the photosensitized rearrangement of **2a** ($5.1 \times 10^{-2} \text{ mol dm}^{-3}$) with 1.0 equiv. of benzophenone in C_6D_6 monitored by 1H NMR spectroscopy and irradiated by a high-pressure mercury lamp through a combination of glass filters ($340 \text{ nm} < \lambda < 380 \text{ nm}$)

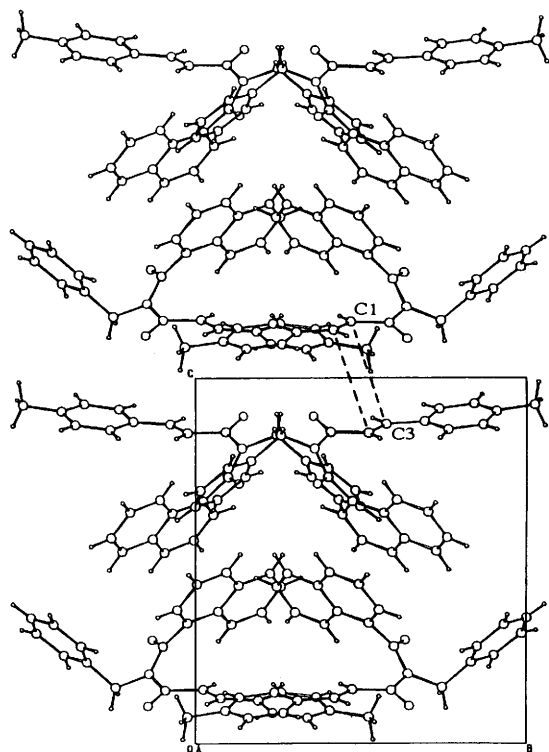


Fig. 3 Packing diagram of **1b**. Intermolecular distance between C-1 and C-3 = 4.34 Å.

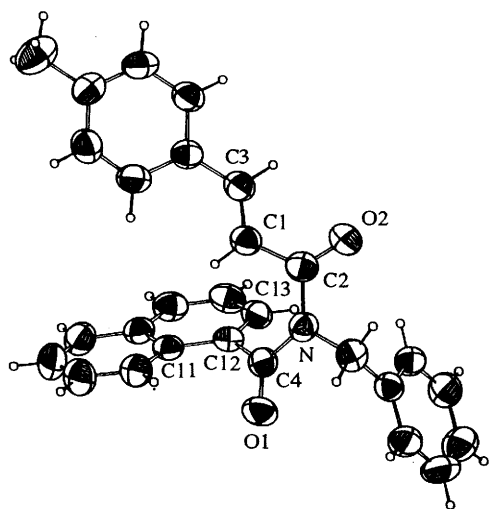


Fig. 4 ORTEP diagram of **1b**

rearrangement with 1.0 equiv. of benzophenone and irradiation through glass filters ($340 \text{ nm} < \lambda < 380 \text{ nm}$). In contrast to the direct irradiation (through Pyrex glass), the formation of **1a** was observed. An increase in diastereoisomeric ratio of the $4\pi + 2\pi$ products (**3a**:**4a**) at 50% conversion from 1.8 (direct irradiation) to 10 (sensitised irradiation) indicates that the direct rearrangement from **2a** to **3a** via one bond scission is favoured under sensitisation.

In contrast to the above-mentioned photocyclisation of **1** in solution, its solid-state photocyclisation afforded the intermolecular $2\pi + 2\pi$ cyclisation products **5** in addition to **2**, **3** and **4**, depending on the substituents at the phenyl group. Powdered monocrystalline **1** was placed between two cover glasses and irradiated for 24 h in a water cooling bath by a high-pressure mercury lamp through a Pyrex glass filter. During the irradiation, melting of the powder was not observed. The dimers **5** were separated by a preparative GPC run. Their stereochemistry was determined to be the α -truxillic

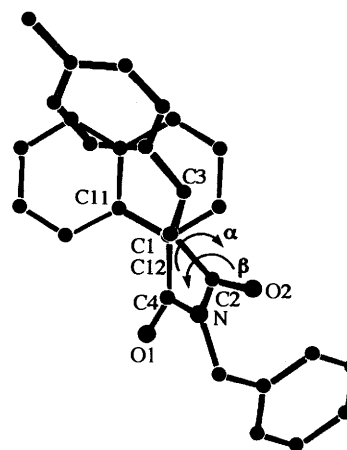


Fig. 5 X-Ray structure of **1b**, viewed from the C-1-C-12 axis. Two possible rotations of the cinnamoyl double bond (C-1-C-3) around the C-1-C-2 single bond are designated as α and β . Hydrogen atoms are omitted for clarity.

Table 3 Yields (%) of cyclisation products in solid state^a

	R ¹	R ²	2	3 + 4 (3:4)	5	1 ^b
1a	H	H	19	33 (60:40)	26	5
1b	Me	H	2	37 (71:29)	48	0
1c	Cl	H	0	42 (67:33)	55	0
1e	Bu ^t	H	99	0	0	0
1f	H	Ph	84	4	0	11

^a Yields after HPLC purification, 24 h irradiation. ^b Recovery of **1**.

acid type from the comparison of their ¹H NMR coupling patterns with those of known α -truxillic acid derivatives and other stereoisomers.⁹ The results are shown in Table 3.

The single crystal X-ray structure analysis of **1b** established that both inter- and intra-molecular cyclisations are possible for this molecule. The packing diagram of **1b** (Fig. 3) shows that the two facing double bonds are located at a distance of 4.34 Å (the intermolecular distance between C-1 and C-3) which is nearly the distance limit for cyclisation.¹⁰ Fig. 4 shows the ORTEP diagram of **1b**. The distances between C-1 and C-12, C-3 and C-13, and C-3 and C-15 are 2.88, 3.94 and 4.95 Å, respectively. The C-1-C-3 double bond is not parallel to the naphthalene ring. Fig. 5 shows the view of **1b** from the C-1-C-12 axis. The styryl moiety has to rotate either clockwise (rotation α) or counterclockwise (rotation β) around the C-1-C-2 single bond to have an efficient π orbital overlap of the naphthyl and the styryl double bonds. The rotation α affords **2b** and **3b**, and the rotation β results in the formation of **4b**. Since the C-1-C-3 double bond has a geometry inclined to the C-12-C-13 double bond, the rotation α should be favoured. From the product distribution, the ratio of the two rotations α : β is calculated to be 2.7 for the intramolecular cyclisation. The bulky substituents ($R^1 = \text{Bu}^t$ and $R^2 = \text{Ph}$) may twist the styryl moiety so that the rotation α is favoured, due to intermolecular steric repulsion ($R^1 = \text{Bu}^t$) or intramolecular repulsion with the neighbouring carbonyl group ($R^2 = \text{Ph}$). The factors which control the *peri*-selectivity for rotation α are obscure. High $2\pi + 2\pi$ selectivity was observed for **1e** and **1f** in the solid state even though the corresponding $4\pi + 2\pi$ cyclisation products were formed in solution. Concerning the selectivity of the inter-/intra-molecular cyclisations, intramolecular cyclisation is preferred with bulky substituents ($R^1 = \text{Bu}^t$ and $R^2 = \text{Ph}$). The introduction of bulky substituents at the phenyl ring could result in an increase in distance between molecular layers by steric repulsion, which would make the intermolecular cyclisation impossible.

It is interesting that a very delicate control by phenyl substituents differentiates the mode of photocyclisation.

Experimental

Melting points were determined on a Yanaco MP-S3 apparatus and are uncorrected. IR spectra were recorded on a Jasco A-202 spectrometer. UV spectra were measured with a Shimadzu model UV-180 spectrometer. ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-FX270, GSX-400 and GSX-500 spectrometers in CDCl_3 with Me_4Si as an internal standard; J values are given in Hz. FAB mass spectra were measured with a Hitachi RMU-7M mass spectrometer. Reaction mixtures were concentrated on a rotary evaporator at 15–20 mmHg. Chromatographic separations were accomplished by flash column chromatography on silica gel (Fuji gel BW 200). Further purification of the reaction products was carried out by a preparative HPLC run; column Merck NH_2 (7 μm , 10 \times 250 mm), hexane–ethyl acetate as eluent. Dimers **5a–d** were separated by a preparative GPC run; column Jaigel H1 (Nippon Bunseki Kohgyo Co.), 20 \times 600 mm, chloroform as eluent.

Procedure for preparation of 1

To a stirred solution of LDA (lithium diisopropylamide) in THF (20 cm^3), prepared from diisopropylamine (5.35 mmol) and butyllithium (5.60 mmol) was added a solution of *N*-benzyl-1-naphthamide (0.653 g, 2.50 mmol) in THF (10 cm^3) at -78°C . After stirring for 15 min, a solution of cinnamoyl chloride (0.420 g, 2.52 mmol) in THF (10 cm^3) was added dropwise and the resulting mixture was gradually warmed to room temp. The reaction was quenched with water (100 cm^3) and the mixture was extracted with benzene (30 $\text{cm}^3 \times 3$). The extracts were dried (MgSO_4) and evaporated and the residue was chromatographed on silica gel using hexane–ethyl acetate (4:1) as eluent to give **1a** (32%, 0.309 g, 0.79 mmol). In a similar manner, amides **1b–f** were prepared.

***N*-Benzyl-*N*-cinnamoyl-1-naphthamide 1a.** Mp $81.5\text{--}83.0^\circ\text{C}$ (from hexane–AcOEt) (Found: C, 82.5; H, 5.25; N, 3.7. $\text{C}_{27}\text{H}_{21}\text{NO}_2$ requires C, 82.84; H, 5.41; N, 3.58%); $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ 220.5 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 38 600) and 280 (2400); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1690, 1656 and 1624; $\delta_{\text{H}}(89.5 \text{ MHz})$ 5.18 (2 H, s), 6.47 (1 H, d, J 18.2), 6.80 (2 H, m), 7.05–8.00 (15 H, m) and 8.39 (1 H, m); $\delta_{\text{C}}(22.4 \text{ MHz})$ 48.27 (t), 121.25 (d), 124.26 (d), 124.44 (d), 126.44 (d), 126.50 (d), 127.27 (d), 127.45 (d), 127.87 (d), 128.26 (d), 128.35 (d), 129.72 (d), 131.45 (d), 133.36 (s), 133.90 (s), 134.16 (s), 137.36 (s), 142.64 (d), 169.16 (s) and 172.41 (s); [Found: MH^+ , 392.1644. $\text{C}_{27}\text{H}_{22}\text{NO}_2$ requires (MH^+), 392.1650].

***N*-Benzyl-*N*-[3-(*p*-tolyl)acryloyl]-1-naphthamide 1b.** Mp $121.0\text{--}121.5^\circ\text{C}$ (from hexane–AcOEt) (Found: C, 82.9; H, 6.1; N, 3.4. $\text{C}_{28}\text{H}_{23}\text{NO}_2$ requires C, 82.94; H, 5.72; N, 3.45%); $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ 220.5 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 17 800) and 281 (3600); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1694, 1656 and 1624; $\delta_{\text{H}}(89.5 \text{ MHz})$ 2.21 (3 H, s), 5.20 (2 H, s), 6.23 (1 H, d, J 15.3), 6.57 (2 H, br d, J 8.1), 6.86 (2 H, br d, J 8.1), 7.20–7.90 (12 H, m) and 8.19 (1 H, m); $\delta_{\text{C}}(22.4 \text{ MHz})$ 21.21 (q), 48.39 (t), 120.32 (d), 124.62 (d), 124.67 (d), 126.59 (d), 126.65 (d), 127.39 (d), 127.66 (d), 128.02 (d), 128.41 (d), 128.53 (d), 129.15 (d), 129.90 (s), 131.33 (s), 131.33 (d), 133.57 (s), 134.40 (s), 137.54 (s), 140.40 (s), 143.06 (d), 169.55 (s) and 172.62 (s) [Found: MH^+ , 406.1807. $\text{C}_{28}\text{H}_{24}\text{NO}_2$ requires (MH^+), 406.1807].

***N*-Benzyl-*N*-[3-(4-chlorophenylacryloyl)-1-naphthamide 1c.** Mp $126.0\text{--}127.0^\circ\text{C}$ (from hexane–AcOEt) (Found: C, 76.0; H, 4.7; N, 3.2. $\text{C}_7\text{H}_20\text{ClNO}_2$ requires C, 76.14; H, 4.73; N, 3.29%); $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ 220.5 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 21 900) and 287.5 (9300); $\delta_{\text{H}}(89.5 \text{ MHz})$ 5.19 (2 H, s), 6.24 (1 H, d, J 15.6), 6.58 (1 H, dt, J 8.5 and 2.2), 7.05 (1 H, dt, J 8.5 and 2.2), 7.18–7.95 (14 H, m) and 8.18 (1 H, m); $\delta_{\text{C}}(22.4 \text{ MHz})$ 48.54 (t), 121.99 (d), 124.47 (d), 124.77 (d), 126.80 (d), 126.88 (d), 127.57 (d), 128.56 (d), 128.66 (d), 128.67 (d), 128.76 (d), 128.82 (d), 129.96 (s), 131.84 (d), 132.67 (s), 133.66 (s), 134.37 (s), 135.89 (s), 137.45 (s), 141.29 (d), 169.28 (s) and 172.21 (s) [Found: MH^+ ,

426.1254 and 428.1228. $\text{C}_{27}\text{H}_{21}^{35}\text{ClNO}_2$ and $\text{C}_{27}\text{H}_{21}^{37}\text{ClNO}_2$ require (MH), 426.1261 and 428.1231].

***N*-Benzyl-*N*-[3-(4-methoxyphenylacryloyl)-1-naphthamide 1d.** Mp $118.0\text{--}119.0^\circ\text{C}$ (from hexane–AcOEt) (Found: C, 79.6; H, 5.45; N, 3.3. $\text{C}_{28}\text{H}_{23}\text{NO}_3$ requires C, 79.79; H, 5.50; N, 3.32%); $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ 219 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 25 000) and 313.5 (6200); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1686, 1638 and 1598; $\delta_{\text{H}}(89.5 \text{ MHz})$ 3.67 (3 H, s), 5.19 (2 H, s), 6.15 (1 H, d, J 15.4), 6.62 (4 H, s), 7.23–7.95 (12 H, m) and 8.19 (1 H, m); $\delta_{\text{C}}(22.4 \text{ MHz})$ 48.48 (t), 55.25 (q), 113.97 (d), 119.07 (d), 124.59 (d), 124.74 (d), 126.63 (d), 126.74 (d), 126.93 (d), 127.45 (d), 128.08 (d), 128.50 (d), 128.62 (d), 129.48 (d), 129.99 (s), 131.57 (d), 133.66 (s), 134.61 (s), 137.67 (s), 143.00 (d), 161.19 (s), 169.76 (s) and 172.74 (s) [Found: MH^+ , 422.1756. $\text{C}_{28}\text{H}_{24}\text{NO}_3$ requires (MH^+), 422.1756].

***N*-Benzyl-*N*-[3-(4-*tert*-butyl)phenylacryloyl]-1-naphthamide 1e.** Mp $150.0\text{--}151.0^\circ\text{C}$ (from hexane–AcOEt) (Found: C, 82.95; H, 6.5; N, 3.1. $\text{C}_{31}\text{H}_{29}\text{NO}_2$ requires C, 83.19; H, 6.53; N, 3.12%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1696, 1654 and 1620; $\delta_{\text{H}}(89.5 \text{ MHz})$ 1.21 (9 H, s), 5.19 (2 H, s), 6.26 (1 H, d, J 15.4), 6.65 (2 H, br d, J 8.3), 7.00–7.95 (14 H, m) and 8.20 (1 H, m); $\delta_{\text{C}}(22.4 \text{ MHz})$ 30.97 (q), 34.66 (s), 48.48 (t), 120.47 (d), 124.56 (d), 124.68 (d), 125.42 (d), 126.71 (d), 127.40 (d), 127.60 (d), 128.05 (d), 128.46 (d), 128.56 (d), 129.99 (s), 131.42 (s), 131.66 (d), 133.63 (s), 134.46 (s), 137.60 (s), 143.20 (d), 153.59 (s), 169.58 (s) and 172.68 (s) [Found: MH^+ , 448.2275. $\text{C}_{31}\text{H}_{30}\text{NO}_2$ requires (MH^+), 448.2277].

***N*-Benzyl-*N*-[3-(3-diphenyl)acryloyl-1-naphthamide 1f.** Mp $134.0\text{--}135.0^\circ\text{C}$ (from hexane–AcOEt) (Found: C, 84.5; H, 5.3; N, 2.95. $\text{C}_{33}\text{H}_{25}\text{NO}_2$ requires C, 84.77; H, 5.39; N, 3.00%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1714 and 1648; $\delta_{\text{H}}(89.5 \text{ MHz})$ 4.89 (2 H, s), 6.14 (1 H, s), 6.13–6.27 (2 H, m), 6.82–7.57 (17 H, m) and 7.80–8.11 (3 H, m); $\delta_{\text{C}}(22.4 \text{ MHz})$ 48.45 (t), 123.13 (d), 124.74 (d), 125.21 (d), 128.02 (d), 128.44 (d), 126.62 (d), 127.51 (d), 127.51 (d), 127.60 (d), 127.72 (d), 127.81 (d), 128.53 (d), 128.61 (d), 129.03 (d), 129.75 (d), 130.29 (s), 131.75 (d), 133.87 (s), 134.91 (s), 137.18 (s), 137.80 (d), 140.07 (s), 149.11 (s), 170.68 (s) and 172.02 (s) [Found: MH^+ , 468.1693. $\text{C}_{33}\text{H}_{26}\text{NO}_2$ requires (MH^+), 468.1693].

Photolysis of 1 in solution

A solution of **1** (0.5 mmol) in benzene (10 cm^3) in a Pyrex test tube (18 mm \times 180 mm) was irradiated with a 400 W high pressure mercury lamp under bubbling argon for 1–7 h. The reaction tube was cooled in a water bucket. After the evaporation of the mixture, the residue was chromatographed on silica gel and further purified by HPLC.

Benzophenone sensitised photorearrangement of 2a

A solution of **2a** in C_6D_6 ($5.1 \times 10^{-2} \text{ mol dm}^{-3}$) in a NMR tube was irradiated with a 400 W high pressure mercury lamp through glass filters (340 nm $< \lambda <$ 380 nm; Toshiba UV-35 + UV-D36A). During irradiation, the ^1H NMR spectrum of the reaction mixture was recorded periodically.

Photolysis of 1 in solid phase

Compound **1** (0.25 mmol) was ground to a powder and then sandwiched between two cover glasses (25 \times 80 mm, thickness 1.5 mm) and dipped in a water bucket. Irradiation was carried out with a 400 W high pressure mercury lamp for 24 h. Dimers **5** were separated from intramolecular cyclisation products by preparative GPC runs. Isomeric products **2** and **3** were separated by preparative HPLC runs.

2-Benzyl-4-phenyl-1,2,3,3a,4,4a-hexahydronaphtho-[1',2':2,3]cyclobuta[1,2-*c*]pyrrole-1,3-dione 2a. Mp $127.0\text{--}127.5^\circ\text{C}$ (from hexane–AcOEt) (Found: C, 82.6; H, 5.3; N, 3.5. $\text{C}_{27}\text{H}_{21}\text{NO}_2$ requires C, 82.84; H, 5.41; N, 3.57%); $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ 218 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 13 400) and 270 (2500); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1768 and 1696; $\delta_{\text{H}}(270 \text{ MHz})$ 3.75 (1 H, d, J 5.4), 3.87 (1 H, ddd, J 9.7, 4.2 and 1.5), 3.95 (1 H, dd,

7.9.2 and 5.4), 4.84 (2 H, s), 5.17 (1 H, dd, *J* 10.0 and 4.2), 6.24 (1 H, dd, *J* 10.0 and 1.5), 6.60 (1 H, br d, *J* 7.3), 6.97 (1 H, dd, *J* 7.3 and 1.5), 7.10 (2 H, dd, *J* 7.4 and 1.6) and 7.04–7.46 (10 H, m); $\delta_{\text{C}}(22.4 \text{ MHz})$ 41.80 (d), 42.08 (t), 47.58 (s), 49.07 (d), 54.41 (d), 123.96 (d), 125.48 (d), 127.63 (d), 127.81 (d), 127.99 (d), 128.17 (d), 128.56 (d), 128.70 (d), 128.79 (d), 129.81 (s), 132.02 (s), 135.92 (s), 136.91 (s), 176.83 (s) and 180.05 (s) [Found: MH^+ , 392.1647. $\text{C}_{27}\text{H}_{22}\text{NO}_2$ requires (MH^+), 392.1650].

(3aR*,4S*)-2-Benzyl-4-phenyl-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[e]isoindole-1,3-dione 3a. Mp 137.0–138.0 °C (from hexane–AcOEt) (Found: C, 82.7; H, 5.4; N, 3.6. $\text{C}_{27}\text{H}_{21}\text{NO}_2$ requires C, 82.84; H, 5.41; N, 3.58%; $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ 222 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 36 800) and 260 (4600); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1774 and 1712; $\delta_{\text{H}}(270 \text{ MHz})$ 2.89 (1 H, d, *J* 7.6), 3.42 (1 H, dd, *J* 7.6 and 1.6), 4.03 (1 H, ddd, *J* 6.4, 1.6 and 1.4), 4.71 (2 H, s), 6.23 (1 H, dd, *J* 7.6 and 1.4), 6.89 (2 H, m), 7.02 (1 H, dd, *J* 7.6 and 6.4), 7.10–7.40 (11 H, m) and 7.77 (1 H, br d, *J* 7.3); $\delta_{\text{C}}(22.4 \text{ MHz})$ 42.24 (t), 44.96 (d), 48.42 (d), 54.56 (s), 57.07 (d), 119.60 (d), 125.94 (d), 126.14 (d), 126.88 (d), 126.94 (d), 127.33 (d), 127.93 (d), 128.53 (d), 128.61 (d), 128.73 (d), 132.31 (d), 136.04 (s), 139.90 (s), 141.21 (s), 141.89 (s), 142.40 (d), 174.83 (s) and 175.13 (s) [Found: MH^+ , 330.1646. $\text{C}_{27}\text{H}_{22}\text{NO}_2$ requires (MH^+), 392.1650].

(3aS*,4R*)-2-Benzyl-4-phenyl-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[e]isoindole-1,3-dione 4a. Obtained as a diastereoisomeric mixture with 3a. Deduced from the spectrum of a mixture with 3a; $\delta_{\text{H}}(270 \text{ MHz})$ 2.97 (1 H, d, *J* 7.6), 3.21 (1 H, dd, *J* 7.6 and 1.6), 4.19 (1 H, br d, *J* 6.4), 4.65 (1 H, d, *J* 15.4), 4.78 (1 H, d, *J* 15.4), 6.62 (2 H, m), 6.91 (1 H, td, *J* 7.7 and 1.4) and aromatic region overlapping with that of 3a; $\delta_{\text{C}}(22.4 \text{ MHz})$ aliphatic and carbonyl carbons 42.36 (t), 45.05 (d), 47.73 (d), 56.89 (s), 58.20 (d), 174.47 (s) and 174.59 (s).

2-Benzyl-4-(*p*-tolyl)-1,2,3,3a,4,4a-hexahydronaphtho[1',2':2,3]cyclobuta[1,2-*c*]pyrrole-1,3-dione 2b. Mp 127.0–128.0 °C (from hexane–AcOEt) (Found: C, 82.7; H, 5.7; N, 3.4. $\text{C}_{28}\text{H}_{23}\text{NO}_2$ requires C, 82.94; H, 5.72; N, 3.45%; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1770 and 1704; $\delta_{\text{H}}(270 \text{ MHz})$ 2.32 (3 H, s), 3.73 (1 H, d, *J* 5.1), 3.87 (1 H, ddd, *J* 9.1, 3.9 and 1.5), 3.93 (1 H, dd, *J* 9.1 and 5.1), 4.87 (2 H, s), 5.23 (1 H, dd, *J* 10.0 and 4.0), 6.29 (1 H, d, *J* 10.0), 6.51 (1 H, dd, *J* 7.5 and 0.8) and 6.95–7.53 (12 H, m); $\delta_{\text{C}}(22.4 \text{ MHz})$ 21.00 (q), 41.97 (d), 42.93 (t), 47.67 (s), 48.96 (d), 54.77 (d), 124.23 (d), 125.57 (d), 127.66 (d), 127.90 (d), 128.14 (d), 128.67 (d), 128.79 (d), 128.85 (d), 128.97 (d), 129.96 (s), 132.17 (s), 133.99 (s), 136.01 (s), 136.88 (s), 177.01 (s) and 180.26 (s) [Found: MH^+ , 406.1799. $\text{C}_{28}\text{H}_{24}\text{NO}_2$ requires (MH^+), 406.1807].

(3aR*,4S*)-2-Benzyl-4-(*p*-tolyl)-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[e]isoindole-1,3-dione 3b. Obtained as a diastereoisomeric mixture with 4b. Deduced from the spectrum of a mixture with 4b; $\delta_{\text{H}}(270 \text{ MHz})$ 2.25 (3 H, s), 2.87 (1 H, d, *J* 7.4), 3.39 (1 H, dd, *J* 7.7 and 1.3), 4.01 (1 H, br d, *J* 6.2), 4.71 (2 H, s), 6.23 (1 H, dd, *J* 7.4 and 1.3), 6.78 (1 H, d, *J* 7.7), 6.98 (1 H, d, *J* 7.7), 7.06 (1 H, dd, *J* 7.4 and 6.2), 7.08–7.38 (11 H, m, aromatic protons overlapping with those of 4b) and 7.75 (1 H, br d, *J* 7.3); $\delta_{\text{C}}(22.4 \text{ MHz})$ aliphatic and carbonyl carbons 20.85 (q), 42.15 (t), 44.54 (d), 48.54 (d), 54.50 (s), 57.01 (d), 174.80 (s) and 175.10 (s).

(3aS*,4R*)-2-Benzyl-4-(*p*-tolyl)-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[e]isoindole-1,3-dione 4b. Obtained as a diastereoisomeric mixture with 3b. Deduced from the spectrum of a mixture with 3b; $\delta_{\text{H}}(270 \text{ MHz})$ 2.82 (s, 3 H), 3.02 (1 H, d, *J* 7.4), 3.20 (1 H, br d, *J* 7.7), 4.20 (1 H, br d, *J* 6.2), 4.63 (1 H, d, *J* 14.6), 4.75 (1 H, d, *J* 14.6), 6.62 (1 H, d, *J* 7.7), 6.66 (1 H, dd, *J* 7.7 and 5.9), 6.91 (1 H, dd, *J* 7.7 and 1.2) and aromatic protons overlapping with those of 3b; $\delta_{\text{C}}(22.4 \text{ MHz})$ aliphatic and carbonyl carbons 20.85 (q), 42.30 (t), 44.63 (d), 47.91 (d), 56.89 (s), 58.04 (d), 174.47 (s) and 174.62 (s).

2-Benzyl-4-(4-chlorophenyl)-1,2,3,3a,4,4a-hexahydronaphtho[1',2':2,3]cyclobuta[1,2-*c*]pyrrole-1,3-dione 2c. Mp

113.0–114.0 °C (from hexane–AcOEt) (Found: C, 75.9; H, 4.7; N, 3.1. $\text{C}_{27}\text{H}_{20}\text{ClNO}_2$ requires C, 76.14; H, 4.73; N, 3.29; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1772 and 1706; $\delta_{\text{H}}(270 \text{ MHz})$ 3.68 (1 H, d, *J* 4.6), 3.87 (1 H, ddd, *J* 9.2, 3.9 and 1.6), 3.92 (1 H, dd, *J* 9.2 and 4.4), 4.86 (2 H, s), 5.16 (1 H, dd, *J* 10.0 and 3.8), 6.30 (1 H, br d, *J* 10.0), 6.61 (1 H, br d, *J* 7.5) and 7.00–7.55 (12 H, m); $\delta_{\text{C}}(22.4 \text{ MHz})$ 41.91 (d), 43.02 (t), 47.64 (s), 48.51 (d), 54.65 (d), 123.57 (d), 125.63 (d), 128.05 (d), 128.14 (d), 128.50 (d), 128.70 (d), 128.89 (d), 129.06 (d), 129.60 (d), 129.72 (s), 131.99 (s), 133.18 (s), 135.63 (s), 135.92 (s), 176.74 (s) and 179.96 (s) [Found: MH^+ , 426.1266 and 428.1229. $\text{C}_{27}\text{H}_{21}^{35}\text{ClNO}_2$ and $\text{C}_{27}\text{H}_{21}^{37}\text{ClNO}_2$ require (MH^+), 426.1261 and 428.1231].

(3aR*,4S*)-2-Benzyl-4-(4-chlorophenyl)-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[e]isoindole-1,3-dione 3c. $\delta_{\text{H}}(270 \text{ MHz})$ 2.83 (1 H, dd, *J* 7.4), 3.39 (1 H, dd, *J* 7.7 and 1.5), 4.00 (1 H, ddd, *J* 6.2, 1.5 and 1.3), 4.72 (2 H, s), 6.25 (1 H, dd, *J* 7.4 and 1.3), 6.83 (1 H, d, *J* 7.7), 7.13–7.43 (11 H, m) and 7.78 (1 H, d, *J* 7.3); $\delta_{\text{C}}(22.4 \text{ MHz})$ 42.27 (t), 44.33 (d), 48.30 (d), 54.48 (s), 57.04 (d), 119.69 (d), 126.08 (d), 126.32 (d), 126.85 (d), 127.99 (d), 128.67 (d), 128.76 (d), 132.40 (d), 132.79 (s), 135.95 (s), 138.58 (s), 140.37 (s), 141.145 (s), 142.19 (d), 174.62 (s) and 174.94 (s) [Found: MH^+ , 426.1262 and 428.1246. $\text{C}_{27}\text{H}_{21}^{35}\text{ClNO}_2$ and $\text{C}_{27}\text{H}_{21}^{37}\text{ClNO}_2$ require (MH^+), 426.1261 and 428.1231].

(3aS*,4R*)-2-Benzyl-4-(4-chlorophenyl)-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[e]isoindole-1,3-dione 4c. Obtained as a diastereoisomeric mixture with 3c. Deduced from the spectrum of a mixture with 3c; $\delta_{\text{H}}(89.5 \text{ MHz})$ 2.96 (1 H, d, *J* 7.4), 3.21 (1 H, dd, *J* 7.7 and 1.3), 4.19 (1 H, dm, *J* 6.2), 4.65 (1 H, d, *J* 15.4), 4.76 (1 H, d, *J* 15.4), 6.62 (2 H, m), 6.91 (1 H, td, *J* 7.7 and 1.4) and aromatic region overlapping with that of 3c; $\delta_{\text{C}}(22.4 \text{ MHz})$ aliphatic and carbonyl carbons 42.42 (t), 44.45 (d), 47.61 (d), 56.86 (s), 58.17 (d), 174.32 (s) and 174.44 (s).

2-Benzyl-4-(4-methoxyphenyl)-1,2,3,3a,4,4a-hexahydronaphtho[1',2':2,3]cyclobuta[1,2-*c*]pyrrole-1,3-dione 2d. Mp 141.0–141.5 °C (from hexane–AcOEt) (Found: C, 79.6; H, 5.4; N, 3.3. $\text{C}_{28}\text{H}_{23}\text{NO}_3$ requires C, 79.79; H, 5.50; N, 3.32%; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1770 and 1702; $\delta_{\text{H}}(270 \text{ MHz})$ 3.69 (1 H, d, *J* 5.2), 3.76 (3 H, s), 3.86 (1 H, ddd, *J* 9.4, 4.0 and 1.5), 3.91 (1 H, dd, *J* 9.4 and 5.2), 4.85 (2 H, s), 5.19 (1 H, dd, *J* 10.1 and 4.0), 6.29 (1 H, br d, *J* 10.1), 6.60 (1 H, br d, *J* 7.4), 6.80 (2 H, d, *J* 8.9) and 6.98–7.51 (10 H, m); $\delta_{\text{C}}(22.4 \text{ MHz})$ 42.06 (d), 42.87 (t), 47.58 (s), 48.60 (d), 55.10 (d and q), 113.61 (d), 124.29 (d), 125.54 (d), 127.63 (d), 127.87 (d), 128.02 (d), 128.23 (d), 128.61 (d), 128.76 (d), 128.82 (d), 129.09 (s), 129.30 (d), 129.93 (s), 132.11 (s), 135.98 (s), 158.69 (s), 176.95 (s) and 180.20 (s) [Found: MH^+ , 422.1754. $\text{C}_{28}\text{H}_{24}\text{NO}_3$ requires (MH^+), 422.1756].

(3aR*,4S*)-2-Benzyl-4-(4-methoxyphenyl)-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[e]isoindole-1,3-dione 3d. $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1776 and 1720; $\delta_{\text{H}}(270 \text{ MHz})$ 2.84 (1 H, d, *J* 7.7), 3.37 (1 H, dd, *J* 7.7 and 1.6), 3.70 (3 H, s), 3.98 (1 H, ddd, *J* 6.2, 1.6 and 1.2), 4.70 (2 H, s), 6.20 (1 H, dd, *J* 7.6 and 1.2), 6.60 (2 H, ddd, *J* 8.9, 2.1 and 2.1), 6.80 (2 H, ddd, *J* 8.9, 2.1 and 2.1), 7.04 (1 H, dd, *J* 7.6 and 6.2), 7.10–7.40 (11 H, m) and 7.76 (1 H, br d, *J* 7.0); $\delta_{\text{C}}(22.4 \text{ MHz})$ 42.12 (t), 44.15 (d), 48.69 (d), 54.48 (s), 55.10 (q), 57.13 (d), 113.82 (d), 119.49 (d), 125.87 (d), 126.02 (d), 126.77 (d), 127.81 (d), 128.23 (d), 128.53 (d), 128.64 (d), 132.02 (s), 133.99 (s), 136.01 (s), 139.00 (s), 141.15 (s), 142.34 (d), 158.39 (s), 174.80 (s) and 175.07 (s) [Found: MH^+ , 422.1748. $\text{C}_{28}\text{H}_{24}\text{NO}_3$ requires (MH^+), 422.1756].

(3aS*,4R*)-2-Benzyl-4-(4-methoxyphenyl)-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[e]isoindole-1,3-dione 4d. Obtained as a diastereoisomeric mixture with 3d. Deduced from the spectrum of a mixture with 3d; $\delta_{\text{H}}(500 \text{ MHz})$ 3.00 (1 H, dd, *J* 7.7), 3.19 (1 H, br d, *J* 7.7), 3.73 (3 H, s), 4.18 (1 H, dm, *J* 6.2), 4.67 (1 H, d, *J* 14.6), 4.75 (1 H, d, *J* 14.6) and aromatic region overlapping with that of 3d.

2-Benzyl-4-(4-*tert*-butylphenyl)-1,2,3,3a,4,4a-hexahydronaphtho[1',2':2,3]cyclobuta[1,2-*c*]pyrrole-1,3-dione 2e. Mp 152.0–

154.0 °C (from hexane–AcOEt); δ_{H} (270 MHz) 1.29 (9 H, s), 3.74 (1 H, d, J 4.9), 3.88 (1 H, ddd, J 8.9, 3.9 and 1.3), 3.92 (1 H, dd, J 8.9 and 4.9), 4.85 (2 H, s), 5.25 (1 H, dd, J 10.0 and 3.9), 6.30 (1 H, br d, J 10.0), 6.58 (1 H, br d, J 7.7) and 6.98–7.52 (12 H, m); δ_{C} (22.4 MHz) 31.20 (q), 34.34 (s), 41.85 (d), 42.84 (t), 47.64 (d), 48.90 (d), 54.80 (d), 124.35 (d), 125.09 (d), 125.45 (d), 127.54 (d), 127.78 (d), 127.90 (d), 127.96 (d), 128.59 (d), 128.70 (d), 129.93 (s), 132.05 (s), 133.90 (s), 135.98 (s), 149.95 (s), 176.83 (s) and 180.17 (s) [Found: MH^+ , 448.2277. $\text{C}_{31}\text{H}_{30}\text{NO}_2$ requires (MH^+), 448.2276].

(3a*R,4*S**)-2-Benzyl-4-(4-*tert*-butylphenyl)-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[*e*]isoindole-1,3-dione 3e.** Obtained as a diastereoisomeric mixture with 4e. Deduced from the spectrum of a mixture with 4e; δ_{H} (270 MHz) 1.23 (9 H, s), 2.85 (1 H, d, J 7.4), 3.39 (1 H, dd, J 7.7 and 1.3), 4.06 (1 H, dt, J 6.2 and 1.3), 4.72 (2 H, s), 6.22 (1 H, dd, J 7.4 and 1.3), 6.85 (2 H, d, J 7.7), 7.07 (1 H, dd, J 7.6 and 6.2), 7.10–7.40 (10 H, m, aromatic protons overlapping with those of 4e) and 7.75 (1 H, dd, J 7.3 and 1.7); δ_{C} (22.4 MHz) aliphatic and carbonyl carbons 31.26 (q), 34.34 (s), 42.21 (t), 44.51 (d), 48.24 (d), 54.53 (s) and 57.22 (d).

(3a*S,4*R**)-2-Benzyl-4-(4-*tert*-butylphenyl)-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[*e*]isoindole-1,3-dione 4e.** Obtained as a diastereoisomeric mixture with 3e. Deduced from the spectrum of a mixture with 3e; δ_{H} (270 MHz) 1.30 (9 H, s), 3.03 (1 H, d, J 7.4), 3.21 (1 H, br d, J 7.7), 4.22 (1 H, br d, J 6.2), 4.65 (1 H, d, J 15.4), 4.76 (1 H, d, J 15.4), 6.62 (1 H, br d, J 7.7), 6.66 (1 H, dd, J 7.7 and 5.9), 6.88 (1 H, td, J 7.3 and 1.1) and aromatic protons overlapping with those of 3e.

2-Benzyl-4,4-diphenyl-1,2,3,3a,4,4a-hexahydronaphtho-[1',2':2,3]cyclobuta[1,2-*c*]pyrrole-1,3-dione 2f. Mp 174.0–175.0 °C (from hexane–AcOEt) (Found: C, 84.6; H, 5.3; N, 3.0. $\text{C}_{33}\text{H}_{25}\text{NO}_2$ requires C, 84.77; H, 5.38; N, 2.99%); ν_{max} (KBr)/ cm^{-1} 1770 and 1706; δ_{H} (270 MHz) 4.33 (1 H, d, J 13.9), 4.45 (2 H, m), 4.53 (1 H, d, J 13.9), 5.37 (1 H, dd, J 10.0 and 5.4), 6.09 (1 H, br d, J 10.0), 6.68 (1 H, dm, J 7.3) and 6.88–7.30 (18 H, m); δ_{C} (22.4 MHz) 42.48 (t), 44.36 (d), 45.38 (s), 58.53 (d), 59.99 (s), 123.99 (d), 125.66 (d), 126.59 (d), 127.15 (d), 127.36 (d), 126.69 (d), 127.75 (d), 127.84 (d), 128.02 (d), 128.50 (d), 128.56 (d), 128.76 (d), 129.87 (s), 132.40 (s), 135.60 (s), 142.01 (s), 142.61 (s), 175.19 (s) and 179.63 (s) [Found: MH^+ , 468.1960. $\text{C}_{33}\text{H}_{26}\text{NO}_2$ requires (MH^+), 468.1964].

***N,N'*-Dibenzyl-*N,N'*-di(1-naphthoyl)-*t*-2,*c*-4-diphenylcyclobutane-*r*-1,*t*-3-dicarboxamide 5a.** ν_{max} (KBr)/ cm^{-1} 1704; δ_{H} (500 MHz) 4.42 (2 H, d, J 15.4), 4.56 (2 H, d, J 15.4), 4.73 (2 H, br m), 4.90 (4 H, dd, J 10.7 and 7.4), 6.50 (4 H, d, J 7.1), 6.69 (2 H, br m), 6.95–7.45 (22 H, m) and 7.76 (4 H, dd, J 7.7 and 3.1); δ_{C} (22.4 MHz) 42.84 (d), 49.16 (t), 51.40 (d), 124.35 (d), 124.71 (d), 126.41 (d), 126.91 (d), 127.12 (d), 127.24 (d), 127.42 (d), 128.11 (d), 128.32 (d), 128.59 (d), 128.73 (d), 129.36 (s), 130.58 (d), 133.27 (s), 133.51 (s), 136.94 (s), 139.77 (s), 172.47 (s) and 174.89 (s) [Found: MH^+ , 783.3234. $\text{C}_{54}\text{H}_{43}\text{N}_2\text{O}_4$ requires (MH^+), 783.3233].

***N,N'*-Dibenzyl-*N,N'*-di(1-naphthoyl)-*t*-2,*c*-4-di(*p*-tolyl)-cyclobutane-*r*-1,*t*-3-dicarboxamide 5b.** ν_{max} (KBr)/ cm^{-1} 1694; δ_{H} (500 MHz) 2.44 (6 H, s), 4.45 (2 H, d, J 15.7), 4.58 (2 H, d, J 15.7), 4.69 (2 H, br m), 4.85 (2 H, dd, J 10.7 and 7.4), 6.51 (4 H, d, J 7.1), 6.75 (2 H, br m), 6.94–7.46 (22 H, m) and 7.76 (4 H, dd, J 8.0 and 3.8); δ_{C} (22.4 MHz) 21.27 (q), 42.42 (d), 49.13 (t), 51.55 (d), 124.32 (d), 124.44 (d), 124.71 (d), 126.38 (d), 126.85 (d), 127.27 (d), 128.05 (d), 128.29 (d), 128.67 (d), 129.21 (d), 129.36 (s), 130.55 (d), 133.30 (s), 133.58 (s), 136.58 (s), 136.82 (s), 137.03 (s), 172.47 (s) and 174.92 (s) [Found: MH^+ , 811.3535. $\text{C}_{56}\text{H}_{47}\text{N}_2\text{O}_4$ requires (MH^+), 811.3536].

***N,N'*-Dibenzyl-*N,N'*-di(1-naphthoyl)-*t*-2,*c*-4-bis(4-chlorophenyl)cyclobutane-*r*-1,*t*-3-dicarboxamide 5c.** ν_{max} (KBr)/ cm^{-1} 1690; δ_{H} (500 MHz) 4.41 (2 H, d, J 15.4), 4.65 (2 H, br m), 4.67 (2 H, d, J 15.4), 4.87 (dd, J 10.7 and 7.4), 6.47 (4 H, d, J 7.4), 6.82 (2 H, br m), 6.95–7.08 (6 H, m), 7.22–7.50 (14 H, m) and 7.79 (4

H, d, J 8.2); δ_{C} (22.4 MHz) 42.18 (d), 49.28 (t), 51.28 (d), 124.05 (d), 124.38 (d), 124.86 (d), 126.56 (d), 127.09 (d), 127.18 (d), 127.54 (d), 128.14 (d), 128.44 (d), 128.64 (d), 129.24 (s), 130.17 (d), 130.85 (d), 133.03 (s), 133.18 (s), 133.27 (s), 136.64 (s), 138.04 (s), 172.62 (s) and 174.32 (s) [Found: MH^+ , 851.2437. $\text{C}_{56}\text{H}_{41}^{35}\text{Cl}_2\text{N}_2\text{O}_4$ requires (MH^+), 851.2443].

(3a*R,4*S**)-2-Benzyl-4,4-diphenyl-1,2,3,3a,4,5-hexahydro-5,9b-ethenobenzo[*e*]isoindole-1,3-dione 3f.** δ_{H} (270 MHz) 3.60 (1 H, dd, J 2.3 and 2.3), 4.53 (1 H, d, J 14.0), 4.62 (1 H, d, J 14.0), 4.66 (1 H, s), 5.57 (1 H, dd, J 10.1 and 2.7), 5.77 (1 H, dd, J 10.1 and 2.7), 6.75 (1 H, dd, J 7.4 and 1.5), 6.95–7.50 (17 H, m) and 8.38 (1 H, d, J 7.7) [Found: MH^+ , 468.1966. $\text{C}_{33}\text{H}_{26}\text{NO}_2$ requires (MH^+), 468.1964].

X-Ray crystal structure determination of 1b

A crystal of 1 from ethyl acetate, with approximate dimensions of 0.40 × 0.30 × 0.20 mm was mounted on a glass fibre and used for the X-ray study.

Crystal data. $\text{C}_{28}\text{H}_{23}\text{NO}_2$, $M = 405.50$. Monoclinic, space group $P2_1/a$, $a = 12.339(3)$, $b = 12.719(1)$, $c = 14.253(3)$ Å, $\beta = 101.38(1)^\circ$, $V = 2192.8 \text{ \AA}^3$, $Z = 2$, $D_c = 1.23 \text{ g cm}^{-3}$. Colourless rods. $F(000) = 856$, $\mu(\text{Mo-K}\alpha) 0.7 \text{ cm}^{-1}$.

Data collection, structure solution and refinement. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-K α radiation (λ 0.710 73 Å) using ω - 2θ scan technique in the range of $2\theta < 46^\circ$. Out of 3359 total reflections, 2372 reflections having intensities greater than $3\sigma(I)$ were used in the refinements. The data were corrected for Lorentz and polarisation factors but no absorption corrections were made. The structure was solved by direct methods using the SPD/VAX (Enraf-Nonius & B. A. Frenz and Associates). Least squares refinement including anisotropic thermal parameters for non-hydrogen atoms and isotropic refinement of hydrogen atoms located in a difference Fourier synthesis terminated at 0.041 (R_w 0.037).

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. For details of the CCDC deposition scheme see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1.

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