Control of the rotational barrier and spatial disposition of the *N*-(2′-methylphenyl) group in succinimides by substituent and solvent effects

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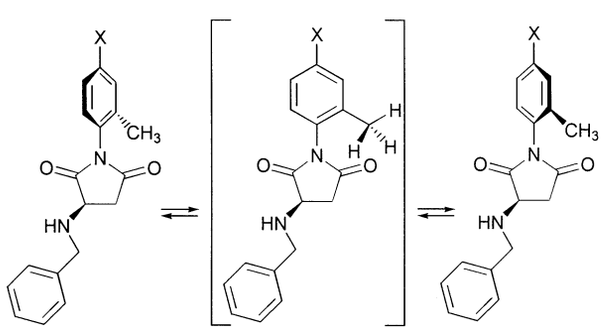
Both the rotational barrier for the *N*-(2′-methylphenyl) group in benzylamino-*N*-(2′-methylphenyl)succinimides 1a–h (X = NEt_2, OMe, Me, H, F, Cl, CO_2Me and NO_2) and the spatial disposition of the *N*-(2′-methylphenyl) group in *N*-(4′-substituted 2′-methylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximides 2a–h (X = NEt_2, OMe, Me, H, F, Cl, CO_2Me and NO_2) are controlled by the substituents present and the solvents used. The rotational barrier of 1 decreases with an increase in σ_p (Hammett's *para* substituent constant of X) and increases in proportion to an increase of the solvent parameter [$E_T(30)$]. Clear correlation was observed in the plots of the *syn/anti* ratio of 2 against σ_m (Hammett's *meta*-substituent constant of X) and the ratios are also controllable by the solvent polarity (μ).

Recently the large rotational barrier around the N–Ar single bond of *N*-phenylimides has been utilised for stereoselective synthesis,[1] molecular recognition[2] and self assembly[3] and for the preparation of functionalised polymers;[4] in the work reported the importance of both the rotational barrier and the spatial disposition of substituents on the *N*-phenyl group was investigated. However, no fundamental study of rotational control has been reported. In this paper, we describe control both of the rotational barrier for the *N*-(2′-methylphenyl) group in succinimide derivatives and the spatial disposition of its methyl group.

Control of the rotational barrier by electrostatic repulsion between the 2′-methyl group and the imide carbonyl groups

The rotational barrier generally consists of the combined effects of steric and electrostatic repulsions, the latter being easier to control than the former. To effect a control system for the rotational barrier based on electrostatic repulsion, we prepared the 4′-substituted 2-benzylamino-*N*-(2′-methylphenyl)succinimides **1** (Scheme 1).[5] The two carbonyls are arranged with pseudo-C_2 symmetry around the rotational axis. The compound exists as a mixture of two rotational isomers **1-A** and **1-C**, which are easily distinguished, each from the other, by ^{1}H NMR chemical shifts for the 2′-methyl group; all the **1-A**/**1-C** ratios were *ca.* 1:1. In the planar state of **1-B** the methyl carbon is closer by 0.7 Å to the carbonyl oxygen (minimum distance of 2.5 Å from AM1 calculation[6]) than the sum of the van der Waals radii of oxygen (1.5 Å) and carbon (1.7 Å).[7] In this short interatomic distance, a large repulsion is expected between the two electronegative atoms (the methyl carbon and carbonyl oxygen). In proportion to an increase/decrease of the electron density of the carbonyl oxygen, the rotational barrier caused by electrostatic interaction must increase/decrease. In the most hindered state **1-B**, the electronic effect from X to the carbonyl oxygens is maximised because of the more effective π-conjugation of the benzene ring with the imide carbonyls. In the stable states **1-A** and **1-C**, the π-conjugation is modified to give perpendicularly twisted structures in which there is a minimum influence of X on the carbonyls. Since the induction effects do not affect the steric repulsion, it is expected that most of the changes in the rotational barrier originates in a change of the electrostatic repulsion in **1-B**.



1a X = NEt_2
1b X = OMe
1c X = Me
1d X = H
1e X = F
1f X = Cl
1g X = CO_2Me
1h X = NO_2

Scheme 1 Rotational isomerisation of **1-A** and **1-C**

Succinimides **1** were prepared from benzylamine and *N*-(2′-methylphenyl)maleimide.[4] The coalescence temperatures (CT) of **1a–h**, calculated from the two 2′-methyl peaks in the ^{1}H NMR spectra, are shown in Table 1.[8] A plot of the rotational barriers $\Delta G^{\ddagger}$ calculated from the CT against Hammett's σ_p substituent constants[9] is shown in Fig. 1. In both [$^2H_6$]-DMSO and [$^2H_8$]toluene $\Delta G^{\ddagger}$ decreases with an increase of the σ_p value for **1a**. The rotational barrier was delicately controlled by the substituent effect. The value in [$^2H_6$]-DMSO is larger than that in [$^2H_8$]toluene. Introduction of electron-withdrawing groups into the 4′-position causes a decrease of electron density on the carbonyl oxygen. As a result, the electrostatic repulsion with the 2′-methyl group in the state **1-B** decreases. On the other hand, electron-donating groups at this position result in an increase of the electron density for the carbonyl oxygen and, subsequently, the electrostatic repulsion increases.

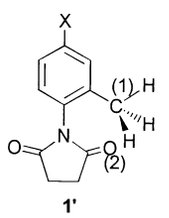
The atomic net charges for 4′-substituted *N*-(2′-methylphenyl)succinimides **1**′ (planar state) were calculated by the AM1 method (Table 2). Although the charge of the methyl carbon changes very little in a series of the derivatives, the charge of the carbonyl oxygen changes by 0.015 from the

Table 1 Hammett's substituent constants and coalescence temperatures in [$^2H_6$]-DMSO and [$^2H_8$]toluene

No.	Compd.	σ_p	CT (K)[a] in [$^2H_6$]-DMSO	CT (K)[a] in [$^2H_8$]toluene
1	**1a**	−0.72	376	—[b]
2	**1b**	−0.27	377	357
3	**1c**	−0.17	373	357
4	**1d**	0	377	359
5	**1e**	+0.06	376	358
6	**1f**	+0.27	369	351
7	**1g**	+0.49	362	347
8	**1h**	+0.78	358	345

[a] Coalescence temperature of 2′-methyl group from the ^1H NMR measurements. Error ±1 °C. [b] The methyl peak of **1a** could not be distinguished from the peak of the solvent (toluene).

Table 2 Net atomic charges of succinimides **1′** calculated by AM1



1'

No.	Compd	X	C(1)	O(2)
1	**1a′**	NEt_2	−0.1791	−0.3033
2	**1b′**	MeO	−0.1810	−0.3054
3	**1c′**	Me	−0.1799	−0.3025
4	**1d′**	H	−0.1807	−0.3018
5	**1e′**	F	−0.1831	−0.3002
6	**1f′**	Cl	−0.1820	−0.2997
7	**1g′**	CO_2Me	−0.1805	−0.2952
8	**1h′**	NO_2	−0.1834	−0.2904

Table 3 Solvent polarity and coalescence temperature for **1d**

No.	Solvent	$E_T(30)$ kcal mol^{-1}	CT (K)[a]
1	[$^2H_8$]Octane	31.1	347
2	[$^2H_8$]Toluene	33.9	359
3	Bromo[$^2H_5$]benzene	36.6	356
4	1,1,2,2-tetrachloro[$^2H_2$]ethane	39.4	371
5	Nitro[$^2H_5$]benzene	42.0	363
6	Di[$^2H_3$]methyl sulfoxide	45.0	377

[a] Solvent polarity parameter (ref. 12). [b] Coalescence temperature for the 2′-methyl group from ^1H NMR measurements. Error ±1 °C.

methoxy- to the nitro-substituted succinimides (from **1b′** to **1h′**). Theoretically, two electronegative sites (carbonyl oxygen and methyl carbon) are at a distance of 2.5 Å in a vacuum, a decrease of 0.015 in charge causes a decrease of 0.4 kcal mol^{-1} in the rotational barrier.[10] The observed values in [$^2H_8$]toluene (0.5 kcal mol^{-1}) and in DMSO (1.2 kcal mol^{-1}) are in good agreement with the calculated values. In **1-B** stabilisation by a CH/O=C interaction is also possible[11] which might be a small part of the change in the rotational barrier.

The possibility that the change in the rotational barrier originates in the double-bond character of the N–Ar single bond was also considered. However, from an AM1 calculation there was no marked change in the length of the N–Ar single bond.

Control of the rotational barrier of **1d** by changing the solvent polarity using the solvent parameter [$E_T(30)$[12]] as an index was attempted (Table 3). The coalescence temperatures are shown in Table 3 and a plot of $\Delta G^{\ddagger}$ against $E_T(30)$ is shown in Fig. 2. The $\Delta G^{\ddagger}$ value was changed by 1.8 kcal mol^{-1} and

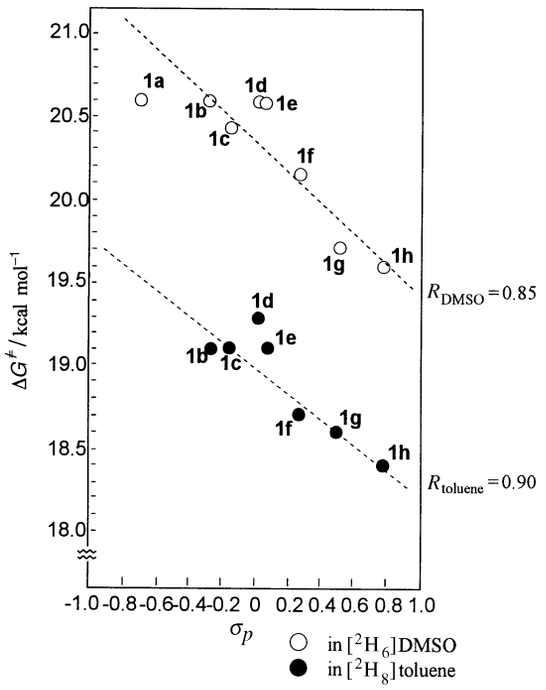


Fig. 1 Plot of rotational barrier ($\Delta G^{\ddagger}$) *vs.* σ_p for *N*-phenylsucciimides **1a–h**

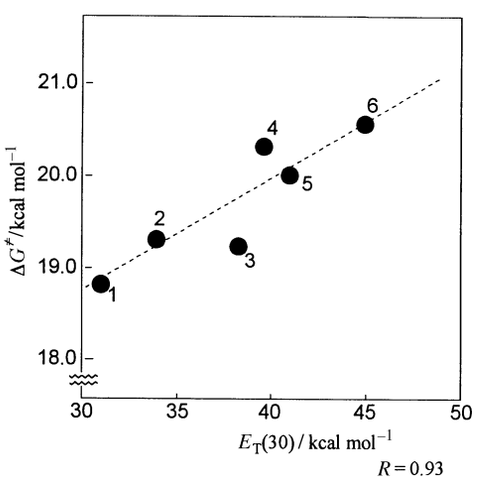


Fig. 2 Plot of rotational barrier ($\Delta G^{\ddagger}$) for **1d** *vs.* the solvent polarity parameter $E_T(30)$. Solvents: 1, [$^2H_{18}$]octane; 2, [$^2H_8$]toluene; 3, [$^2H_5$]-bromobenzene; 4, 1,1,2,2-tetrachloro[$^2H_2$]ethane; 5, nitro[$^2H_5$]benzene; and 6, [$^2H_6$]-DMSO.

increased with an increase in $E_T(30)$. In the state **1-B**, the electrostatic repulsion between the carbonyl oxygen and the methyl carbon may increase in polar solvents due to the withdrawal of the π-electrons of the *N*-phenyl by the imide carbonyl oxygen. In this simple system, the rotational barrier could be controlled variably by the solvent polarity.

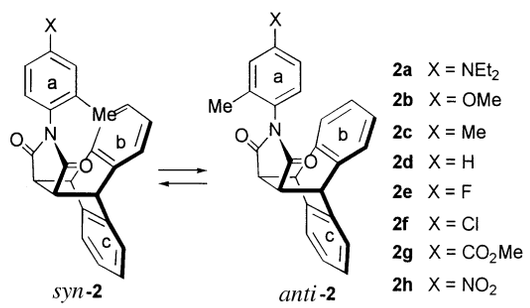
It became clear that the rotational barrier around Ar–N single bond in *N*-(2′-methylphenyl)succinimides was delicately controlled by the electron density of the carbonyl oxygen.

Control of the spatial disposition of the 2′-methyl group on the *N*-phenyl group by intra- and inter-molecular CH/π interactions

In recent years, CH/π interactions have been recognised as of importance in molecular recognition,[13] evidence for their existence having been reported from X-ray crystallographic analyses of sulfoxides[14] and cobalt[15] and manganese complexes.[16] The existence of CH/π interactions in the crystalline state is difficult to prove, however, because the packing achieved is the result of several interactions. Interactions of CH with ethylene[17,18] and

benzene [19,20] were confirmed by calculation, the maximum value being 1 kcal mol^{-1}.[19] For the measurement of these weak interactions, rotational isomerisation is a suitable probe, which has been used to measure an edge-to-face and a face-to-face π–π interactions between phenyl groups.[21] Experimental investigations of CH/π interactions were also attempted in the conformational isomerisation of triptycene[22] and isopropyl(phenylethyl)ketone derivatives.[23] However, during such isomerisation the benzene ring simultaneously experiences both CH/π interaction with the hydrogen and electrostatic repulsion with the electronegative atoms present. In such a system, the CH/π interaction could not be separated from other electrostatic repulsions. In our system the influence of other electrostatic repulsions was minimised as far as possible. In this way we established spatial control of the 2′-methyl group of the *N*-phenyl group by CH/π interactions.

To realise the control system, we designed *N*-(2′-methylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximides **2a**–**h** (Scheme 2). To investigate CH/π interaction between the



Scheme 2 Rotational isomerisation of *syn*-**2** and *anti*-**2**

methyl hydrogen and the π electrons of the benzene ring (b), the electron density of the *N*-phenyl group was varied by an introduction of substituent X at the *para* position. The molecule shows two isomers *syn*-**2** and *anti*-**2** which are in equilibration. In *syn*-**2** the distance between the centre of the benzene ring and the methyl carbon was estimated from an MM2 calculation to be 3.51 Å, the distance appropriate for CH/π interaction.[19] If the positive charge of the methyl hydrogen increases/decreases, the CH/π interaction must increase/decrease. During the isomerisation, the distance between the benzene ring (b) and X remains constant, because X is centred on the rotational axis of the N–Ph single bond. Accordingly, electrostatic repulsion between the benzene ring (b) and X is kept constant during the rotation.

The succinimides **2** were prepared by Diels–Alder reaction of *N*-(2′-methylphenyl)maleimides with anthracene.[24,25] At room temperature the rotational isomerisation around the N–Ar bond is so slow that both isomers can be observed by ^{1}H NMR spectroscopy (the rotational barrier around N–Ar is 20–21 kcal mol^{-1}). The *syn/anti* ratios can be measured using the integration of the singlet peaks of the 2′-methyl groups of both isomers since these peaks were well separated. The 2′-methyl group of *syn*-**2** appeared 1 ppm upfield of that of *anti*-**2**. In the series of **2a**–**h** the isomer ratios were investigated in [$^2H_4$]-chloroform and [$^2H_6$]-DMSO and Fig. 3 shows a plot of their values against σ_m (Hammett-*meta*-substituent constants). A clear correlation was observed in the plots. A weak substituent effect is observed in [^{2}H]chloroform. In contrast, the isomer ratios were changed from 43:57 for **2a** to 70:30 for **2h** in [$^2H_6$]-DMSO. This change in the ratios means the *syn*-**2** became 0.67 kcal mol^{-1} more stable as a result of the substituent effect in this series (from **2a** to **2h**). Substitution with an electron-withdrawing group increased the ratio. The net atomic charges of the methyl protons in **2**′a–**h** calculated by AM1 and Hammett's substituent constants (σ_m) are shown in Table 4. The imide **2**′ has a perpendicularly twisted structure. The proton H_a is in the same plane as the *N*-phenyl group. In Scheme 2, the

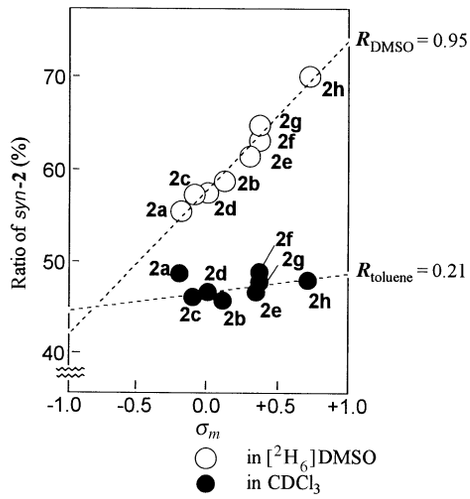
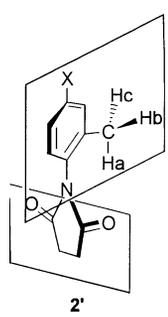


Fig. 3 Plot of ratio of *syn*-**2** *vs.* Hammett's substituent constant (σ_m)

Table 4 Net atomic charges of 2′-methyl hydrogens in succinimides **2**′ calculated by AM1



2'

No.	Compd	X	σ_m	H_a	H_b, H_c	Average
1	**2a**′	NEt_2	−0.21	+0.0801	+0.0899	+0.0866
2	**2c**′	Me	−0.07	+0.0803	+0.0896	+0.0865
3	**2d**′	H	0.0	+0.0808	+0.0897	+0.0867
4	**2b**′	MeO	+0.12	+0.0835	+0.0908	+0.0884
5	**2e**′	F	+0.34	+0.0848	+0.0942	+0.0911
6	**2f**′	Cl	+0.37	+0.0835	+0.0932	+0.0900
7	**2h**′	CO_2Me	+0.37	+0.0837	+0.0932	+0.0900
8	**2h**′	NO_2	+0.71	+0.0874	+0.0984	+0.0947

proton H_a is that nearest to the benzene ring (b) in *syn*-**2**. The net atomic charge of H_a is increasing (Δq = 0.0073 from **2a**′ to **2h**′) with an increase of σ_m. According to Coulomb's law this means that *syn*-**2** becomes 0.3 kcal mol^{-1} (in a vacuum) more stable than *anti*-**2** by changing the substituents X from NEt_2 to NO_2.

To investigate the solvent effect on the CH/π interaction, the *syn/anti* ratios of **2d** and **2h** were measured in several solvents ([$^2H_6$]benzene, [^{2}H]chloroform, [$^2H_5$]pyridine and [$^2H_6$]-DMSO). The polar solvents gave larger ratios than the non-polar ones (Fig. 4). The nitro group of **2h** effectively withdraws the electrons of the 2′-methyl hydrogens in the polar solvents to become more positive. This brings about a stronger CH/π interaction between the hydrogen and the π-electrons of the benzene ring (b) and gives rise to larger *syn/anti* ratios.

The crystal structure of **2h** was measured by X-ray analysis (see Fig. 5); the compound was crystallised from benzene. From the intramolecular CH/π interaction its stereochemistry was expected to be *syn*. However, the obtained structure was an *anti*-form (*anti*-**2h**). After detailed examination of the packing structure, it was found that there is intermolecular CH/π interaction of the methyl(C-25) hydrogens with the benzene rings [b (C8-13) and c (C1-6)] of the neighbouring molecule (Fig. 6). The benzene ring (b) uses its downside face for intermolecular

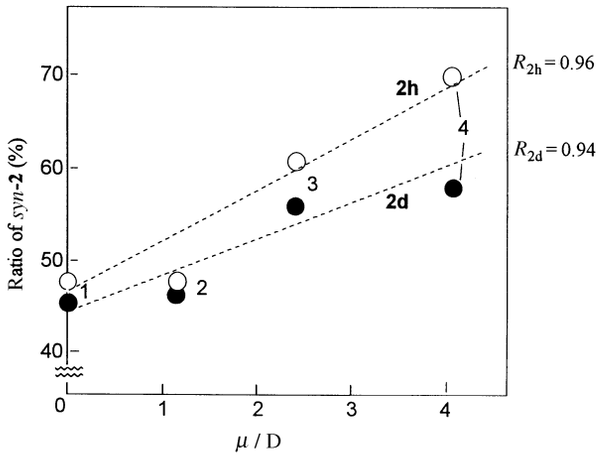


Fig. 4 Plot of ratio of *syn*-**2** *vs.* dipole moment (μ). Solvents: 1, [$^2H_6$]-benzene; 2, [^{2}H]chloroform; 3, [$^2H_5$]pyridine; 4, [$^2H_6$]-DMSO.

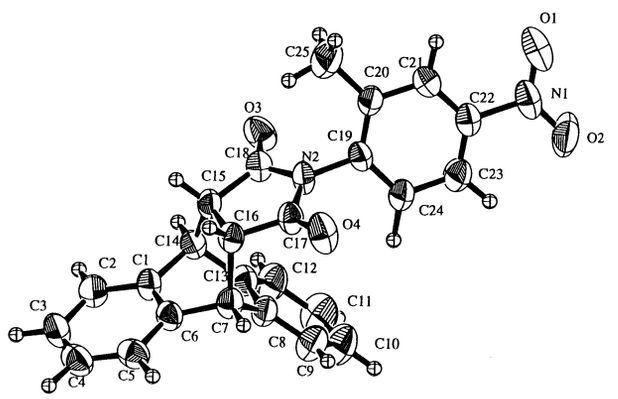


Fig. 5 The single-crystal X-ray structure of **2h**

CH/π interaction, the upside face not being involved in the crystal packing at all. The distances between the methyl carbon and the plane of the benzene rings b and c are *ca.* 3.7 and 3.8 Å, respectively [the sum (3.8 Å) of the van der Waals radii of methyl group (2.0 Å) and aromatic carbon (1.8 Å)[6,14]]. The molecules were linearly arranged in the crystal as a result of the intermolecular CH/π interactions. Intra- and inter-molecular CH/π interaction may compete during the packing process. Thus, although there is a preference for intermolecular interaction, where the molecules are so disposed and the intermolecular distance such that CH/π interaction occurs, intramolecular interaction is favoured in solution because of the greater distances between the molecules. Thus the direction of *N*-(2′-methylphenyl) group of the imide is controllable by varying the strength of the CH/π interaction.

Conclusion

In this study it has been confirmed that the rotational barrier of the *N*-phenyl group and its substituent's spatial disposition can be controlled by the electronic effects of the substituents or solvents. This means that the molecule's rotational behaviour can also be controlled by polarisation in an electric field.

Experimental

Mps are uncorrected. ^{1}H NMR (270 MHz) and ^{13}C NMR (22.4 MHz) spectra were recorded in $CDCl_3$ and were referenced against internal tetramethylsilane. Chemical shifts are reported in parts per million (δ units). High-performance liquid chromatography (HPLC) was performed with Merck Lichrosorb Si 60 column (7 μm). Flash column chromatography was

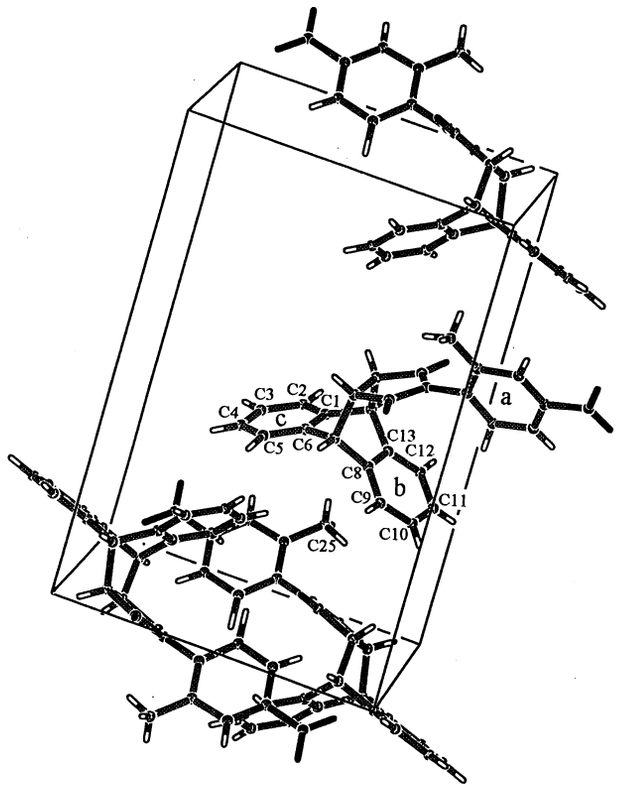


Fig. 6 Unit cell packing of **2h**

performed with Fuji silica gel BW-200 (200 mesh). All solvents were freshly distilled and stored over molecular sieves 4 Å. All maleimides were prepared from maleic anhydride and *p*-substituted *o*-toluidines by the usual method.

A typical procedure for synthesis of 3-benzylamino-*N*-(4′-substituted 2′-methylphenyl)maleimides 1a–h

To a solution of *N*-(2′-methylphenyl)maleimide (1.10 mmol) in benzene (10 cm^3) was added to a solution of benzylamine (1.2 equiv.) in benzene (10 cm^3) and the mixture was stirred at room temperature for 5 days. The reaction was quenched by the addition of water (10 cm^3) to the mixture after which it was diluted with ethyl acetate (20 cm^3) and stirred. The organic phase was separated with aqueous $NaHCO_3$, dried ($MgSO_4$) and concentrated. The products were separated by column chromatography on silica gel eluting with hexane–ethyl acetate (1.5:1). Further purification was effected by HPLC eluting with hexane–ethyl acetate (1.5:1) to give **1d** (0.870 mmol).

3-Benzylamino-*N*-(4-diethylamino-2-methylphenyl)-succinimide 1a. Yield 84%; oil; ν_{max}(neat)/cm^{-1} 3322 (NH), 3026 (CH), 2966 (CH), 2926 (CH), 1719 (C=O), 1703 (C=O), 1610, 1512, 1376, 1269 and 1190; δ_H(270 MHz; $CDCl_3$) 1.15 (t, *J* 6.9, 6 H), 1.95 (br, 1 H), 2.03 (s, 1.5 H), 2.09 (s, 1.5 H), 2.69 (dd, *J* 18.1 and 5.4, 0.5 H), 2.70 (dd, *J* 18.1 and 5.4, 0.5 H), 3.00 (dd, *J* 18.1 and 8.2, 0.5 H), 3.03 (dd, *J* 18.1 and 8.2, 0.5 H), 3.33 (q, *J* 6.9, 4 H), 3.88 (d, *J* 13.6, 0.5 H), 3.90 (d, *J* 13.6, 0.5 H), 3.92 (dd, *J* 8.2 and 5.4, 0.5 H), 3.93 (dd, *J* 8.2 and 5.4, 0.5 H), 3.96 (d, *J* 13.6, 1 H), 6.46–6.58 (m, 2 H), 6.78–6.91 (m, 1 H) and 7.29–7.42 (m, 5 H); δ_C(22.4 MHz; $CDCl_3$) 12.41 (q), 18.11 (q), 36.28 (t), 36.42 (t), 44.12 (t), 51.52 (2), 51.70 (t), 55.40 (d), 55.64 (d), 109.49 (d), 112.80 (d), 112.92 (d), 117.81 (s), 127.27 (d), 128.14 (d), 128.44 (d), 135.51 (s), 135.92 (s), 138.67 (s), 148.25 (s), 174.83 (s), 174.98 (s), 177.48 (s) and 177.57 (s) [Found (HRMS/EI): *m/z* 366.2196. Calc. for $C_{18}H_{18}N_3O_4$ (MH^+): 366.2181].

3-Benzylamino-*N*-(4′-methoxy-2′-methylphenyl)succinimide 1b. Yield 76%; white crystals; mp 81.0–82.5 °C (diethyl ether) (Found: C, 70.29; H, 6.17; N, 8.59. $C_{19}H_{20}N_2O_3$ requires C,

70.35; H, 6.22; N, 8.64%); ν_{max}(KBr)/cm^{-1} 3320 (NH), 1708 (C=O), 1612, 1254 and 1184; δ_H(270 MHz; $CDCl_3$) 2.01 (br, 1 H), 2.08 (s, 1.5 H), 2.13 (s, 1.5 H), 2.71 (dd, *J* 18.1 and 5.3, 0.5 H), 2.72 (dd, *J* 18.1 and 5.3, 0.5 H), 3.02 (dd, *J* 18.1 and 8.2, 0.5 H), 3.04 (dd, *J* 18.1 and 8.2, 0.5 H), 3.80 (s, 3 H), 3.88 (d, *J* 12.6, 0.5 H), 3.89 (d, *J* 12.6, 0.5 H), 3.93 (dd, *J* 8.2 and 5.3, 0.5 H), 3.95 (dd, *J* 8.2 and 5.3, 0.5 H), 3.96 (d, *J* 12.6, 1 H), 6.78–6.87 (m, 2 H), 6.90– 7.02 (m, 1 H) and 7.21–7.48 (m, 5 H); δ_C(22.4 MHz; $CDCl_3$) 17.75 (q), 36.31 (t), 36.45 (t), 51.49 (t), 51.64 (t), 55.16 (q), 55.40 (d), 55.64 (d), 112.06 (d), 112.15 (d), 116.17 (d), 123.13 (s), 123.18 (s), 127.33 (d), 128.11 (d), 128.47 (d), 128.59 (s), 128.82 (d), 136.52 (s), 136.97 (s), 138.55 (s), 159.94 (s), 174.29 (s), 174.44 (s), 177.01 (s) and 177.10 (s).

3-Benzylamino-*N*-(2′,4′-dimethylphenyl)succinimide 1c. Yield 92%; oil; ν_{max}(neat)/cm^{-1} 3322 (NH), 3026 (CH), 2924 (CH), 2858 (CH), 1781, 1710 (C=O), 1455, 1385 and 1186; δ_H(270 MHz; $CDCl_3$) 1.95 (br, 1 H), 2.07 (s, 1.5 H), 2.13 (s, 1.5 H), 2.35 s, 3 H), 2.71 (dd, *J* 17.8 and 5.3, 0.5 H), 2.73 (dd, *J* 17.8 and 5.3, 0.5 H), 3.03 (dd, *J* 17.8 and 8.4, 0.5 H), 3.05 (dd, *J* 17.8 and 8.4, 0.5), 3.87 (d, *J* 13.7, 0.5 H), 3.89 (d, *J* 13.7, 0.5 H), 3.95 (dd, *J* 8.4 and 5.3, 0.5 H), 3.96 (d, *J* 13.7, 1 H), 3.97 (dd, *J* 8.4 and 5.3, 0.5 H), 6.90 (d, *J* 7.7, 0.5 H), 6.98 (d, *J* 7.7, 0.5 H), 7.05–7.17 (m, 2 H) and 7.20–7.49 (m, 5 H); δ_C(22.4 MHz; $CDCl_3$) 17.42 (q), 20.94 (q), 36.40 (t), 36.51 (t), 51.49 (t), 51.64 (t), 55.46 (d), 55.73 (d), 127.33 (d), 127.48 (d), 127.96 (s), 128.14 (d), 128.47 (d), 131.66 (d), 131.75 (d), 134.76 (s), 135.21 (s), 138.61 (s), 139.39 (s), 174.14 (s), 174.29 (s), 176.89 (s) and 176.95 (s) [Found (HRMS/FAB): *m/z* 309.1627. Calc. for $C_{19}H_{21}N_2O_2$: 309.1627].

3-Benzylamino-*N*-(2′-methylphenyl)succinimide 1d. Yield 79%; oil; ν_{max}(neat)/cm^{-1} 3322 (NH), 3064 (CH), 3028 (CH), 2928, 2862, 1780, 1719 (C=O), 1498 and 1383; δ_H(270 MHz; $CDCl_3$) 2.09 (br, 1 H), 2.12 (s, 1.5 H), 2.18 (s, 1.5 H), 2.73 (dd, *J* 18.1 and 5.3, 0.5 H), 2.74 (dd, *J* 18.1 and 5.3, 0.5 H), 3.04 (dd, *J* 18.1 and 8.3, 0.5 H), 3.06 (dd, *J* 18.1 and 8.3, 0.5 H), 3.89 (d, *J* 12.7, 0.5 H), 3.90 (d, *J* 12.7, 0.5 H), 3.95 (dd, *J* 8.3 and 5.3, 0.5 H), 3.97 (dd, *J* 8.3 and 5.3, 0.5 H), 3.97 (d, *J* 12.7, 0.5 H) and 6.99–7.48 (m, 9 H); δ_C(22.4 MHz; $CDCl_3$) 17.60 (q), 36.45 (t), 51.58 (t), 51.70 (t), 55.46 (d), 55.79 (d), 126.85 (d), 127.54 (d), 127.60 (d), 127.69 (d), 127.93 (d), 128.29 (d), 128.61 (d), 128.91 (s), 129.51 (d), 130.61 (s), 130.67 (s), 131.03 (d), 131.15 (s), 135.24 (s), 135.72 (s), 138.25 (s), 138.40 (s), 173.96 (s), 174.11 (s), 176.62 (s) and 176.77 (s) [Found (HRMS/FAB): 295.1437. Calc. for $C_{18}H_{19}N_2O_2$: 295.1446].

3-Benzylamino-*N*-(4′-fluoro-2′-methylphenyl)succinimide 1e. Yield 84%; oil; ν_{max}(neat)/cm^{-1} 3326 (NH), 3062 (CH), 2928 (CH), 2856, 1781, 1719 (C=O), 1710 (C=O), 1455, 1417, 1390, 1242 and 1192; δ_H(270 MHz; $CDCl_3$) 2.02 (br, 1 H), 2.10 (s, 1.5 H), 2.17 (s, 1.5 H), 2.72 (dd, *J* 18.1 and 5.2, 0.5 H), 2.73 (dd, *J* 18.1 and 5.2, 0.5 H), 3.04 (dd, *J* 18.1 and 8.2, 0.5 H), 3.06 (dd, *J* 18.1 and 8.2, 0.5 H), 3.88 (d, *J* 12.3, 0.5 H), 3.90 (d, *J* 12.3, 0.5 H), 3.94 (dd, *J* 8.2 and 5.2, 0.5 H), 3.96 (dd, *J* 8.2 and 5.2, 0.5 H), 3.97 (d, *J* 12.3, 1 H), 6.90–7.11 (m, 3 H) and 7.13–7.40 (m, 5 H); δ_C(22.4 MHz; $CDCl_3$) 17.63 (q), 36.31 (t), 36.42 (t), 51.43 (t), 51.55 (t), 55.37 (d), 55.61 (d), 113.70 (d), 117.65 (d), 126.41 (s), 126.47 (s), 127.33 (d), 128.08 (s), 128.44 (d), 129.36 (d), 129.60 (d), 137.85 (s), 138.30 (s), 138.49 (s), 162.51 (s), 173.81 (s), 173.96 (s) and 176.65 (s) [Found (HRMS/FAB): *m/z* 313.1366. Calc. for $C_{18}H_{18}N_2O_2F$: 313.1353].

3-Benzylamino-*N*-(4′-chloro-2′-methylphenyl)succinimide 1f. Yield 41%; oil; ν_{max}(neat)/cm^{-1} 3324 (NH), 3026 (CH), 2924 (CH), 1729, 1714 (C=O), 1695, 1384, 1179 and 699; δ_H(270 MHz; $CDCl_3$) 1.92 (br, 1 H), 2.10 (s, 1.5 H), 2.16 (s, 1.5 H), 2.73 (dd, *J* 18.4 and 5.4, 0.5 H), 2.74 (dd, *J* 18.4 and 5.4, 0.5 H), 3.04 (dd, *J* 18.4 and 8.0, 0.5 H), 3.05 (dd, *J* 18.4 and 8.0, 0.5 H), 3.88 (d, *J* 13.9, 0.5 H), 3.90 (d, *J* 13.9, 0.5 H), 3.95 (dd, *J* 8.0 and 5.4, 0.5 H), 3.96 (dd, *J* 8.0 and 5.4, 0.5 H), 3.96 (d, *J* 13.9, 1 H), 6.98 (d, *J* 9.1, 0.5 H), 7.04 (d, *J* 9.1, 0.5 H) and 7.18–7.46 (m, 7 H); δ_C(22.4 MHz; $CDCl_3$) 17.63 (q), 36.00 (t), 36.72 (t), 51.73 (t), 51.85 (t), 55.58 (d), 55.85 (d), 127.12 (d), 127.63 (d), 128.26 (d), 128.67 (d), 129.06 (d), 129.15 (s), 129.27 (d), 131.09 (d), 131.18 (d), 135.33 (s), 137.27 (s), 137.74 (s), 138.43 (s), 173.79 (s), 173.96 (s), 176.56 (s) and 176.65 (s) [Found (HRMS/FAB): *m/z* 329.1038. Calc. for $C_{18}H_{18}N_2O_2Cl$: 329.1096].

3-Benzylamino-*N*-(4′-methoxycarbonyl-2′-methylphenyl)-succinimide 1g. Yield 54%; oil; ν_{max}(neat)/cm^{-1} 3322 (NH), 3060 (CH), 3026 (CH), 2950 (CH), 1780 (C=O), 1712 (C=O), 1585 and 1458; δ_H(270 MHz; $CDCl_3$) 2.00 (br, 1 H), 2.17 (s, 1.5 H), 2.22 (s, 1.5 H), 2.65 (dd, *J* 18.1 and 5.2, 0.5 H), 2.66 (dd, *J* 18.1 and 5.2, 0.5 H), 3.06 (dd, *J* 18.1 and 8.3, 0.5 H), 3.08 (dd, *J* 18.1 and 8.3, 0.5 H), 3.90 (d, *J* 16.7, 0.5 H), 3.92 (d, *J* 16.7, 0.5 H), 3.93 (s, 3 H), 3.95 (d, *J* 16.7, 1 H), 3.97 (dd, *J* 8.3 and 5.2, 0.5 H), 3.96 (dd, *J* 8.3 and 5.2, 0.5 H), 7.12 (d, *J* 8.3, 0.5 H), 7.19 (d, *J* 8.3, 0.5 H), 7.26–7.41 (m, 5 H) and 7.92–8.04 (m, 2 H); δ_C(22.4 MHz; $CDCl_3$) 17.72 (q), 36.69 (t), 36.78 (t), 51.70 (t), 51.85 (t), 52.24 (q), 55.67 (d), 55.94 (d), 127.60 (d), 128.08 (d), 128.26 (d), 128.67 (d), 131.09 (s), 131.15 (s), 132.34 (d), 132.40 (s), 134.73 (s), 134.79 (s), 135.78 (s), 136.25 (s), 138.46 (s), 166.18 (s), 173.58 (s), 173.73 (s) and 176.41 (s) [Found (HRMS/FAB): *m/z* 353.1519. Calc. for $C_{18}H_{18}N_2O_2Cl$: 353.1470].

3-Benzylamino-*N*-(2′-methyl-4′-nitrophenyl)succinimide 1h. Yield 41%; oil; ν_{max}(neat)/cm^{-1} 3322 (NH), 3028 (CH), 2928 (CH), 2854, 1786, 1722 (C=O) and 1529; δ_H(270 MHz; $CDCl_3$) 2.05 (br, 1 H), 2.23 (s, 1.5 H), 2.30 (s, 1.5 H), 2.87 (dd, *J* 18.2 and 5.0, 0.5 H), 2.88 (dd, *J* 18.2 and 5.0, 0.5 H), 3.08 (dd, *J* 18.2 and 8.2, 0.5 H), 3.12 (dd, *J* 18.2 and 8.2, 0.5 H), 3.91 (d, *J* 14.0, 0.5 H), 3.93 (d, *J* 14.0, 0.5 H), 3.99 (dd, *J* 8.2 and 5.0, 0.5 H), 4.02 (dd, *J* 8.2 and 5.0, 0.5 H), 7.13–7.42 (m, 6 H) and 8.09–8.25 (m, 2 H); δ_C(22.4 MHz; $CDCl_3$) 18.02 (q), 36.66 (t), 36.72 (t), 51.67 (t), 51.79 (t), 55.58 (d), 55.88 (d), 121.90 (d), 125.99 (d), 126.05 (d), 127.66 (d), 128.23 (d), 128.91 (s), 129.12 (d), 137.65 (s), 138.19 (s), 138.25 (s), 148.01 (s), 173.16 (s), 173.31 (s), 175.99 (s) and 176.05 (s) [Found (HRMS/EI): *m/z* 353.1293. Calc. for $C_{18}H_{18}N_3O_4$ (MH^+): 340.1295].

Typical procedure for the synthesis of *N*-(4′-substituted 2′-methylphenyl)-9,10-ethanoanthracene-11,12-dicarboximides 2a–h

A mixture of *N*-(2′-methylphenyl)maleimide (0.478 mmol), anthracene (1 equiv.) and xylene (20 cm^3) was refluxed for 2 h after which the xylene was replaced with ethyl acetate (20 cm^3). The solution was washed with aqueous $NaHCO_3$, dried ($MgSO_4$) and concentrated. Column chromatography of the residue on silica gel eluting with hexane–ethyl acetate (4:1) gave *N*-(2′-methylphenyl)-9,10-ethanoanthracene-11,12-dicarboximide **2d**.

***N*-(4′-Diethylamino-2′-methylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximide 2a.** Yield 45%; white crystals; mp 229–230 °C (benzene) (Found: C, 79.42; H, 6.35; N, 6.43. $C_{29}H_{28}N_2O_2$ requires C, 79.78; H, 6.46; N, 6.41%); ν_{max}(KBr)/cm^{-1} 2966, 1710, 1607, 1516, 1468, 1379, 1269, 1190, 1108, 965 and 760; δ_H(270 MHz; $CDCl_3$) 0.98 (s, 1.5 H), 1.10 (t, *J* 6.9, 6 H), 1.98 (s, 1.5 H), 3.26 (q, *J* 6.9, 2 H), 3.27 (q, *J* 6.9, 2 H), 3.35–3.38 (m, 2 H), 4.86–4.93 (m, 2 H), 5.58 (s, *J* 8.9, 0.5 H), 6.21–6.30 (m, 1 H), 6.36–6.43 (m, 1 H), 6.70 (d, *J* 8.9, 0.5 H), 7.10–7.29 (m, 4 H) and 7.30–7.45 (m, 4 H); δ_C(22.4 MHz; $CDCl_3$) 12.53 (q), 16.97 (q), 18.20 (q), 44.24 (t), 45.38 (d), 45.85 (d), 46.93 (d), 109.34 (d), 109.58 (d), 112.62 (d), 112.83 (d), 117.90 (s), 118.05 (s), 124.14 (d), 124.26 (d), 125.21 (d), 125.42 (s), 126.65 (s), 126.74 (s), 127.03 (s), 127.21 (s), 127.84 (s), 128.32 (s), 135.69 (s), 136.37 (s), 138.91 (s), 139.33 (s), 141.47 (s), 142.10 (s), 148.28 (s), 176.65 (s) and 176.74 (s).

***N*-(4′-Methoxy-2′-methylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximide 2b.** Yield 45%; white crystals; mp 265–267 °C (benzene) (Found: C, 78.96; H, 5.27; N, 3.42. $C_{26}H_{21}NO_3$ requires C, 78.96; H, 5.35; N, 3.54%); ν_{max}(KBr)/cm^{-1} 2940, 1774, 1710, 1612, 1506, 1459, 1377, 1252 and 770; δ_H(270 MHz; $CDCl_3$) 1.00 (s, 1.4 H), 2.00 (s, 1.6 H), 3.33–3.42 (m, 2 H), 3.70 (s, 1.6 H), 3.71 (s, 1.4 H), 4.82–4.94 (m, 2 H), 5.42 (d, *J* 8.7, 0.5 H), 6.50–6.74 (m, 2 H), 6.83 (d, *J* 8.7, 0.5

H) and 7.10–7.51 (m, 8 H); δ_C(22.4 MHz; $CDCl_3$) 16.58 (q), 17.84 (q), 45.32 (d), 45.82 (d), 47.05 (d), 55.28 (q), 111.97 (d), 112.12 (d), 115.99 (d), 123.24 (s), 123.36 (s), 124.17 (d), 124.29 (d), 125.18 (d), 125.42 (d), 126.71 (d), 126.80 (d), 127.09 (d), 127.30 (d), 128.29 (d), 128.70 (d), 136.70 (s), 137.42 (s), 138.88 (s), 139.27 (s), 141.29 (s), 141.92 (s), 159.97 (s), 176.20 (s) and 176.29 (s).

***N*-(2′,4′-Dimethylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximide 2c.** Yield 30%; white crystals; mp 223–225 °C (benzene) (Found: C, 83.20; H, 5.70; N, 3.33. $C_{26}H_{21}NO_2 \cdot 0.5C_6H_6$ requires C, 83.22; H, 5.78; N, 3.34%); ν_{max}(KBr)/cm^{-1} 3018, 2958, 2918, 1773, 1711, 1508, 1458, 1380 and 1187; δ_H(270 MHz; $CDCl_3$) 1.01 (s, 1.4 H), 2.02 (s, 1.6 H), 2.24 (s, 1.6 H), 2.26 (s, 1.4 H), 3.35–3.42 (m, 2 H), 4.84–4.91 (m, 2 H), 5.39 (d, *J* 7.9, 0.5 H) and 6.74–6.95 (m, 10.5); δ_C(22.4 MHz; $CDCl_3$) 16.20 (q), 17.42 (q), 20.97 (q), 45.29 (d), 45.79 (d), 47.08 (d), 124.11 (d), 124.23 (d), 125.15 (d), 125.39 (d), 126.65 (d), 126.74 (d), 126.74 (d), 126.94 (d), 127.03 (d), 127.24 (d), 127.39 (d), 127.51 (d), 127.90 (s), 128.05 (s), 131.36 (d), 131.57 (d), 134.91 (s), 135.60 (s), 138.82 (s), 139.24 (s), 139.33 (s), 141.29 (s), 141.92 (s), 175.96 (s) and 176.05 (s).

***N*-(2′-Methylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxiimide 2d.**[23c] Yield 70%.

***N*-(4′-Fluoro-2′-dimethylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximide 2e.** Yield 83%; white crystals; mp 251–253 °C (benzene) (Found: C, 78.18; H, 4.58; N, 3.57. $C_{25}H_{18}NO_2F$ requires C, 78.31; H, 4.73; N, 3.65); ν_{max}(KBr)/cm^{-1} 2928, 1774, 1714, 1501, 1384 and 1193; δ_H(270 MHz; $CDCl_3$) 1.01 (s, 1.4 H), 2.05 (s, 1.6 H), 3.39–3.42 (m, 2 H), 4.87–4.92 (m, 2 H), 5.44 (dd, *J* 6.6 and 4.1, 0.5 H), 6.68–6.95 (m, 2.5 H) and 7.10–7.48 (m, 8 H); δ_C(22.4 MHz; $CDCl_3$) 16.50 (q, *J* 1.3), 17.75 (q, *J* 1.3), 45.29 (d), 45.82 (d), 47.11 (d), 113.58 (d, *J* 22.7), 113.85 (d, *J* 22.7), 117.40 (d, *J* 22.7), 117.55 (d, *J* 22.7), 124.20 (d), 124.32 (d), 125.21 (d), 125.45 (d), 126.50 (s, *J* 2.7), 126.77 (d), 126.85 (d), 127.15 (d), 127.36 (d), 129.06 (d, *J* 9.4), 129.48 (d, *J* 9.4), 138.03 (s, *J* 8.7), 138.80 (s, *J* 8.7), 141.15 (s), 141.80 (s), 157.11 (s), 168.15 (s), 175.84 (s) and 175.93 (s).

***N*-(4′-Chloro-2′-methylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximide 2f.** Yield 69%; white crystals; mp 178–179.5 °C (benzene) (Found: C, 75.08; H, 4.54; N, 3.32. $C_{25}H_{18}NO_2Cl$ requires C, 75.09; H, 4.53; N, 3.50%); ν_{max}(KBr)/cm^{-1} 3074, 3026, 2956, 2922, 1775, 1710, 1490, 1468, 1399, 1379, 1214, 1192, 1162 and 763; δ_H(270 MHz; $CDCl_3$) 1.01 (s, 1.5 H), 2.02 (s, 1.5 H), 3.37–3.42 (m, 2 H), 4.83–4.92 (m, 2 H), 5.41 (d, *J* 8.3, 0.5 H), 6.85 (d, *J* 8.3, 0.5 Hz) and 6.96–7.54 (m, 10 H); δ_C(22.4 MHz; $CDCl_3$) 16.32 (q), 17.57 (q), 45.32 (d), 45.82 (d), 47.17 (d), 124.20 (d), 124.32 (d), 125.21 (d), 125.45 (d), 126.77 (d), 126.88 (d), 127.03 (d), 127.15 (d), 127.36 (d), 128.61 (d), 129.06 (d), 129.18 (s), 129.27 (s), 130.67 (d), 130.85 (d), 135.09 (s), 137.36 (s), 138.07 (s), 138.82 (s), 139.24 (s), 141.12 (s), 141.77 (s) and 175.63 (s).

***N*-(4′-Methoxycarbonyl-2′-methylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximide 2g.** Yield 44%; white crystals; mp 261–262.5 °C (benzene) (Found: C, 76.61; H, 4.93; N, 3.26. $C_{27}H_{21}NO_4$ requires C, 76.58; H, 4.99; N, 3.30%); ν_{max}(KBr)/cm^{-1} 2956, 1777, 1715, 1381, 1287, 1267, 1211 and 765; δ_H(270 MHz; $CDCl_3$) 1.10 (s, 1.4 H), 2.11 (s, 1.6 H), 3.40–3.46 (m, 2 H), 3.87 (s, 1.6 H), 3.88 (s, 1.4 H), 4.88–4.94 (m, 2 H), 5.57 (d, *J* 8.3 Hz, 0.5 H), 7.01 (d, *J* 8.3, 0.5 H), 7.10–7.48 (m, 8 H) and 7.63–7.91 (m, 2 H); δ_C(22.4 MHz; $CDCl_3$) 16.38 (q), 17.60 (q), 45.29 (d), 45.79 (d), 47.26 (d), 52.18 (q), 124.17 (d), 124.32 (d), 125.18 (d), 125.42 (d), 126.77 (d), 126.85 (d), 127.18 (d), 127.36 (d), 127.54 (d), 127.72 (d), 128.02 (d), 128.32 (d), 130.88 (d), 131.93 (d), 132.11 (d), 134.76 (s), 135.86 (s), 136.58 (s), 138.76 (s), 139.18 (s), 141.09 (s), 141.74 (s), 166.15 (s), 175.40 (s) and 175.52 (s).

***N*-(2′-Methyl-4′-nitrophenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximide 2h.** Yield 71%; white crystals; mp 215–217 °C (benzene) (Found: C, 73.09; H, 4.27; N, 6.82. $C_{25}H_{18}N_2O_4$ requires C, 73.16; H, 4.42; N, 6.82%); ν_{max}(KBr)/cm^{-1} 3072, 3062, 3038, 2964, 1722, 1529, 1380 and 1162; δ_H(270 MHz; $CDCl_3$) 1.16 (s, 1.4 H), 2.19 (s, 1.6 H), 3.43–3.48 (m, 2 H), 4.86–4.94 (m, 2 H), 5.65 (d, *J* 8.5, 0.5 H), 7.11 (d, *J* 8.5, 0.5 H), 7.16–7.48 (m, 8 H) and 7.81–8.12 (m, 2 H); δ_C(22.4 MHz; $CDCl_3$) 16.76 (q), 17.93 (q), 45.32 (d), 45.82 (d), 47.37 (d), 121.60 (d), 121.90 (d), 124.23 (d), 124.38 (d), 125.24 (d), 125.48 (d), 125.63 (d), 125.81 (d), 126.88 (d), 127.00 (d), 127.27 (d), 127.45 (d), 128.70 (d), 129.15 (d), 136.40 (s), 137.83 (s), 138.52 (s), 138.79 (s), 139.15 (s), 140.91 (s), 141.56 (s), 147.95 (s), 175.07 (s) and 175.22 (s).

Crystal data

$C_{25}H_{18}N_2O_4$, $M = 410.43$, monoclinic, $a = 11.283$ (2) Å, $b = 16.103$ (2) Å, $c = 11.391$ (1) Å, $\beta = 102.76$ (1)°, $V = 2018.6$ (5) Å^3, space group $P2_1/n$ (No. 14), $Z = 4$, $D_x = 1.350$ g cm^{-3}. Colourless prismatic crystals; crystal dimensions 0.45 × 0.08 × 0.48 mm, μ(Cu-Kα) = 7.59 cm^{-1}.

Data collection and processing

Rigaku AFC5S diffractometer, $\omega/2\theta$ mode with ω scan width = 1.31 + 0.30 tan θ, ω scan speed 16.0 deg min^{-1}, graphite-monochromated Cu-Kα ($\lambda = 1.541\,78$ Å) radiation; 3302 reflections measured, 3128 unique (max., min. transmission factors = 1.00, 0.62), giving 1993 with $I > 3.00\sigma(I)$.

Structure analysis and refinement

The structure was solved by direct methods using SIR88 and refined by full-matrix least-squares techniques using DIRDIF94. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but their positions were not refined. The position of the hydrogens was determined by calculation. The final residuals for reflections with $I > 3.00\sigma(I)$ were $R = 0.067$, $wR = 0.074$.

Full details of the crystallographic results have been deposited with the Cambridge Crystallographic Data Centre.† Any requests for this material should be accompanied by a full bibliographic citation together with the reference no. CCDC 207/91.

† Details of the scheme are given in Instructions for Authors (1997), *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1.

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