Sterically Hindered Free Radicals. Part 22.[1] Dimerization and EPR Spectroscopy of Indanedionyl and 9-Acylfluorenyl Radicals

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2-Phenylindanedionyl radicals **5a**, their *p*- and *o*-monosubstituted derivatives and related compounds **5b–h** recombine by C–C bond formation giving **6a–h**. In contrast, *o*-substituted derivatives **5i–k** and the 2-*tert*-butylindanedionyl radicals **5l** react to give the enol ethers **10a–d** by C–O coupling. The EPR data indicate that the substituents are more bulky in **5i–l** than in **5a–h**. From the proton splitting constants it is concluded that **5a** is planar and **5h** nearly planar (twist angle of the phenyl group *ca.* 30°). The phenyl group in **5i** is twisted considerably with an angle of about 50°. The *g* values of **5i–k** are larger than those of **5a–h** indicating a higher spin density in the carbonyl groups.

9-Acylfluorenyl radicals **12b–c**, representing the planar conformations of diarylmethyl radicals **1c**, **d**, give no enol ethers like **4**, but recombine by C–C bond formation yielding **13b–c**. Their *g* values indicate that the acyl groups are twisted out of the radical plane.

Since it has been found that 'hexaphenylethane' is really a quinonoid dimer **2** of the trityl radical **1**,[2] there has been a continuous discussion regarding why and how sterically hindered radicals dimerize.[3,4] In the case of diarylmethyl radicals $Ar_2C^{\bullet}$–R **1**, the structure of their dimers (if there are any) depends on the nature of both Ar and R.[5] Several diphenyl derivatives give quinonoid dimers **2**, whereas a simple blocking of the 4-positions (the other substituents remaining the same) can result in α,α-dimers **3**.[5,6] As an example, the diphenyl(methoxycarbonyl)methyl radical **1a** forms the quinoid dimer **2a**, whereas radicals **1b** recombine to give **3b**, see Scheme 1. In contrast to this, **12a** which might be regarded as a fixed planar conformation of **1a** shows C–C coupling to form **13a**. It is obvious that small differences in the radical structure drastically influence the recombination behaviour. If the steric strain is enlarged further (Ar_2 = Mes_2 or Ph, Mes in **1f**, **g**), the radicals are monomers.[7,‡] If Ar is Ph and R is acyl, enol ethers **4** are formed.[5] The radicals recombine *via* the mesomeric oxyl form as well as the carbon centred form. This is consistent with EPR

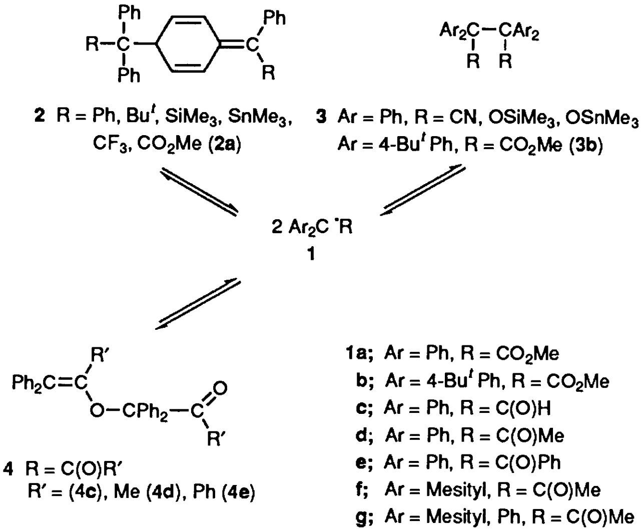
$$Ph_2C^{\bullet}\text{–}C(R)\text{=}O \longleftrightarrow Ph_2C\text{=}C(R)\text{–}O^{\bullet}$$

results. The high *g* values of α-carbonyl radicals generally show an important contribution of the oxyl form.[3,8,9] The sterical hindrance is shown by the low *o*- and *p*-proton splittings in **1** indicating that the phenyl groups are twisted out of the radical plane.[9–11] In contrast to this, dibenzoylphenyl radicals **1′e** dimerize by C–C coupling to give **3′e**.[7,9,§]

$$\underset{\mathbf{1'e}}{2[Ph(CO)]_2C^{\bullet}Ph} \rightleftharpoons \underset{\mathbf{3'e}}{[Ph(CO)]_2PhC\text{–}CPh[(CO)Ph]_2}$$

To allow a more detailed investigation of the influence of bulky substituents in α-carbonyl radicals, some related radicals with bridged substituents will be described.

The 2-phenylindanedionyl radical **5a** might be treated as a fixed planar conformation of radicals **1′e**. Many derivatives of **5a** were prepared, see Scheme 2, and the structure of their dimers, as well as the EPR data, will be presented and discussed.



Scheme 1

Additionally, data for the *tert*-butylindanedionyl radical **5i** will be given below.

An important field of free radical research is offered by the indane-1,3-dionyls **5**. Earlier synthetic work had targeted the dimers **6**,[12,14] starting from an aldehyde **7** and phthalide **8** giving the indane-1,3-diones **9** whose oxidation led to the dimers **6**. Reversible dissociation of the latter giving **5** was noticed qualitatively in the few cases investigated so far.[14,15] Attention has been given to the possible competition between C–C and C–O recombination of **5a**, and the ethane-like structure **6a** has been found.[13] EPR data are known only for **5f** and related dialkylaminophenylindanedionyl radicals.[14,15] However, because of the complexity of the spectra, the results have to be regarded with care. Completing our results concerning **12a**,[5] we have now generated the 9-acylfluorenyl radicals **12b**, **c**, and studied the structure of their dimers; the EPR data are reported here.

Results and Discussion

The dimers of the indane-1,3-dionyls **5a–l** have been prepared, as shown in Scheme 2, and by analogous procedures.[12–15] For

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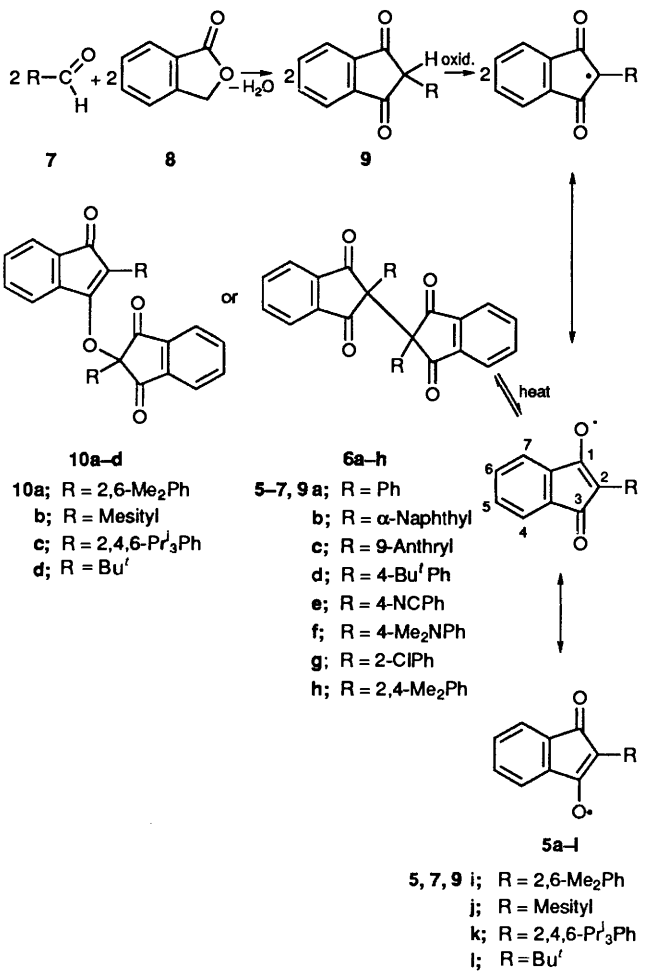
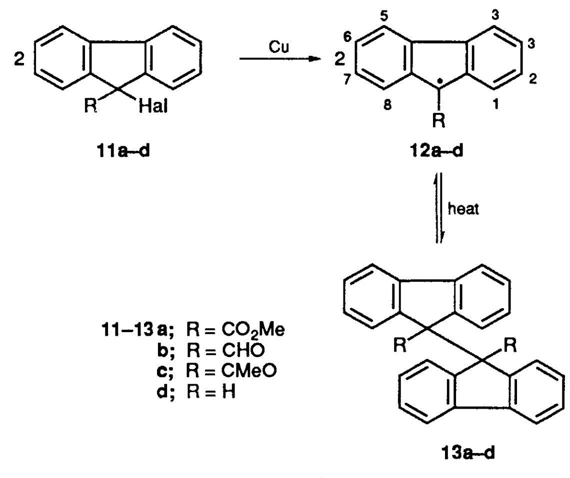
‡ The complex EPR spectra of the radicals **1f**, **g** have not been analysed.

§ **3′e**: $\delta_H(CDCl_3)$ 7.1–7.4 (m, 30 H, ArH); $\delta_C(CDCl_3)$ 94.52 (*C*COPh), 126.24–130.82 (HC_{ar}), 133.44, 135.37 (C_{ar}) and 184.04 (CO).



Scheme 2



Scheme 3

determining the structure of the dimers, we looked for the vinyl ether bands in their IR spectra. These have been found with **10a–d** which proved their enol ether structure but could not be observed with **6a–h** which makes their ethane-like structure likely. In most cases, this conclusion has been confirmed by ^{1}H and ^{13}C NMR spectroscopy, see Experimental section.

EPR data of **5a–h** are listed in Table 1 together with the experimental conditions. The spectra appeared during heating the probes to the given temperatures and disappeared again after cooling, indicating a reversible radical–dimer equilibrium. Because of this, the radical concentration is strongly dependent on the temperature. The *T* values given in the Table were chosen in such a way that the concentrations were high enough to get spectra which could easily be interpreted. ENDOR studies have been performed under the same conditions, but without success. In addition we tried to get ENDOR spectra at lower temperatures after rapidly cooling the probes to temperatures near the melting point of the solvents, also without success. The results of INDO calculations for **5a** and **5i** are also presented. Figs. 1(*a*) and 2(*a*) show EPR spectra of **5a** and **5i**, Figs. 1(*b*) and 2(*b*) show simulated spectra which had been calculated using the values given in Table 1.

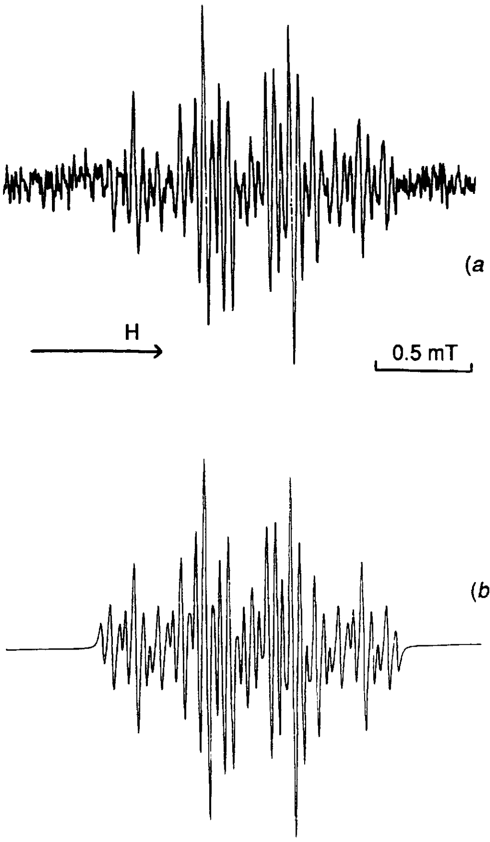


Fig. 1 EPR Spectrum of **5a** (*a*) and its simulation (*b*) computed with the data given in Table 1

During heating of **6a** up to 150 °C in Ph_2O, a weak EPR signal of **5a** can be observed which disappears after 20 min, probably due to consecutive reactions. The spectrum shows a large doublet (0.478 mT) of triplets (0.390 mT) of triplets (0.131 mT) of triplets (0.058 mT). The first three couplings are smaller by 30% than the splittings of the ring protons of the benzyl radical[16,17] and similar to those of the phenyl group in **1′e**,[9] and are assigned to the phenyl protons of **5a**. The relation $|\rho_p/\rho_m| = 3.65$ points to a planar configuration of **5a**.[10,11,18] The small coupling is presumably due to two protons of the indanedionyl moiety.

As support for the reported assignment of the splitting constants to the indane protons in **5a**, spin densities in the 2-phenylindanedionyl system have been calculated. By means of a MNDO RHF program[19] the geometry of the latter has been optimized. An INDO calculation[20] has been carried out with the structure obtained in this way. The result was a twist angle of the phenyl group of about 90° with respect to the indanedionyl residue. The corresponding splitting constants were not in agreement with the measured values. Thus, in a second calculation a planar conformation of the Ph residue was assumed. The results are given in Table 1. The observed

Table 1 EPR data for indanedionyl radicals **5a–l** and related radical **1′e**

Radical	a (H)/mT	g	Dimer	Solvent	T/K
5a	o: 0.390; m: 0.131; p: 0.478 4,7 (indane): 0.058	2.0032	**6a**	Ph_2O	460
a	o: −0.515; m: 0.318; p: −0.484 4,7 (indane): 0.058; 5,6 (indane): 0.026				
5b			**6b**	Ph_2O	>423
5c		2.0038	**6c**	Ph_2O	473
5d	o: 0.375; m: 9.125	2.0038	**6d**	Ph_2O	456
5e	o: 0.400; m: 0.200; N: 0.478 4,7 (indane): 0.056	2.0038	**6e**	Ph_2O	454
5f	o: 0.272; m: 0.067; N: 0.361 Me: 0.317 (6 H); 5,6 (indane): 0.043 4,7 (indane): 0.025[b]	2.0033	**6f**	PhH	333
5g		2.0038	**6g**	Ph_2O	421
5h	o: 0.228 (3 H), 0.338 (1 H) m: 0.165; p: 0.456 (3 H); 4,7 (indane): 0.062	2.0039	**6h**	Ph_2O	433
5i	o: 0.124 (6 H); m: 0.155; p 0.186 4,7 (indane): 0.062	2.0041	**10a**	PhH	350
c	o: −0.734; m: 0.394; p: −0.526 4,7 (indane): 0.050; 5,6 (indane): 0.009				
d	o: −0.275; m: 0.288; p: −0.206 4,7 (indane): 0.060; 5,6 (indane): 0.026				
e	o: −0.164; m: 0.245; p: −0.130 4,7 (indane): 0.062; 5,6 (indane): 0.026				
5j	o: 0.128 (6 H); m: 0.153; p: 0.256 (3 H) 4,7 (indane): 0.051	2.0044	**10b**	PhH	353
5k		2.0045	**10c**	PhMe	338
5l	Bu^t(9 H) = 4,7 (indane): 0.063	2.0045	**10d**	PhH	328
1′e[f]	o: 0.397; m: 0.138; p: 0.471 4 H: 0.015	2.0035	**3′e**	Ph_2O	423

[a] INDO calculation for a planar system **5a**. [b] In CCl_4 at 343 K.[15] [c–e] INDO calculations for a twisted system **5i** with twist angles of 10° (*c*), 50° (*d*) and 60° (*e*) [f] From ref. 9. The small coupling is presumably due to the *o*-benzoyl protons.

splittings for the two indane protons apparently have to be assigned to the protons in the positions 4 and 7. The assignment is not unambiguous; a simple HMO–McLachlan calculation leads to a contrary result. Whereas, in the 2-Ph residue, the *p*-proton splittings are reproduced very well, the *o*- and the *m*-splittings are not calculated exactly. The relation of the ring proton splittings correspond to those calculated with INDO for the benzyl radical with a planar conformation.[21] The g value of **5a** (2.0032) is higher than that of the benzyl radical (2.0026) and similar to that of the unbridged radical **1′e** (2.0035) indicating a comparable contribution of the oxyl forms of **5a** and **1′e** which also recombine by C–C bond formation.[7,9]

Compounds **5b**, **c** show weak EPR spectra with many lines which have not been analysed. The g value of **5c** is similar to that of **5a**. The EPR spectra of **5d**, **e**, like **5a**, show weak signals above 150 °C, being poorly resolved for **5d**. The EPR spectrum of **5f** has been observed by dissociation of the dimer at only 60 °C, g = 2.0033. Its splitting constants are known, and an HMO–McLachlan spin density calculation has been performed based on a planar conformation, with satisfying results.[15] The dimer is now confirmed to be **6f**, its low dissociation temperature of 60 °C is remarkable. Apparently a stronger stabilization of **5f** by mesomerism involving its amino group is given. For certain other cases, a 'capto-dative' stabilization has been suggested,[22] but has been questioned as a general concept.[23]

The radicals **5g**, **h** with an *o*-Cl or *o*-Me substituent at the 2-Ph residue likewise give C–C recombination yielding **6g**, **h**. The multiline EPR spectrum of **5g** has not been analysed.

The EPR spectrum of **5h** shows a doublet (0.338 mT) of two triplets (0.062 mT, 0.165 mT) of two quartets (0.228 mT, 0.456 mT). The smaller triplet is assigned to two indanedionyl ring protons, in accordance with **5a**, the smaller quartet to the *o*-methyl protons by analogy with the proton splittings in the *o*- and *p*-methylbenzyl radicals.[16] The observed decrease of $|\rho_p/\rho_m|$ from 3.65 in **5a** to about 2.4 in **5h** shows a deviation of the phenyl group from planarity, comparable with that in the trityl radical ($|\rho_p/\rho_m|$ = 2.5[16]) with a twist angle of about 30°. This is in contrast to the conformation of the *o*-methylbenzyl radicals which are assumed to be planar ($|\rho_p/\rho_m|$ = 3.53[16]). The g values of all the radicals **5a**–**h** are in the range 2.003–2.004 indicating a similar mixing of the oxyl form to the distribution of the electron spin density in these radicals. This is consistent with the observation that **5a**–**h** dimerize in the same way, by C–C recombination.

A different situation has been found for the radicals **5i**–**k**, bearing two methyl or isopropyl substituents in *o*-position of the 2-Ph residue. Their dimers have an enol structure **10a**–**c**, and dissociate at lower temperatures, see Table 1. The EPR spectrum of **5i** given in Fig. 1(b) clearly shows the absence of a large coupling expected to be present at about 0.4 mT. The value of 0.186 mT obtained by simulation of the spectrum and a_m = 0.155 mT gives $|\rho_p/\rho_m|$ = 1.20. The low value indicates an appreciable twist of the aryl ring. As a support for this interpretation, INDO calculations for **5i** were carried out using twist angles of 10°, 50° and 60°. The actual angle apparently can be found near to the 60° value, if the *p*-proton splitting is taken as a measure for twisting. The splitting constants of **5j** are comparable with those of **5i**. The EPR signal of **5k** could not be interpreted because of its poor resolution. The g values of **5i**–**k** are larger than 2.004 indicating an increased contribution of the oxyl form. This is explained by the twist of the phenyl group out of the radical plane which lowers the mesomeric interaction between the indane and the phenyl system. The dimer has an enol type structure, this is explained by the higher steric hindrance of *tert*-butyl at the radical C centre compared with the phenyl group which prevents C–C recombination. This is in accordance with the E^S_C values describing the steric hindrance of substituents which are larger for *tert*-butyl (E^S_C = 1.54) than

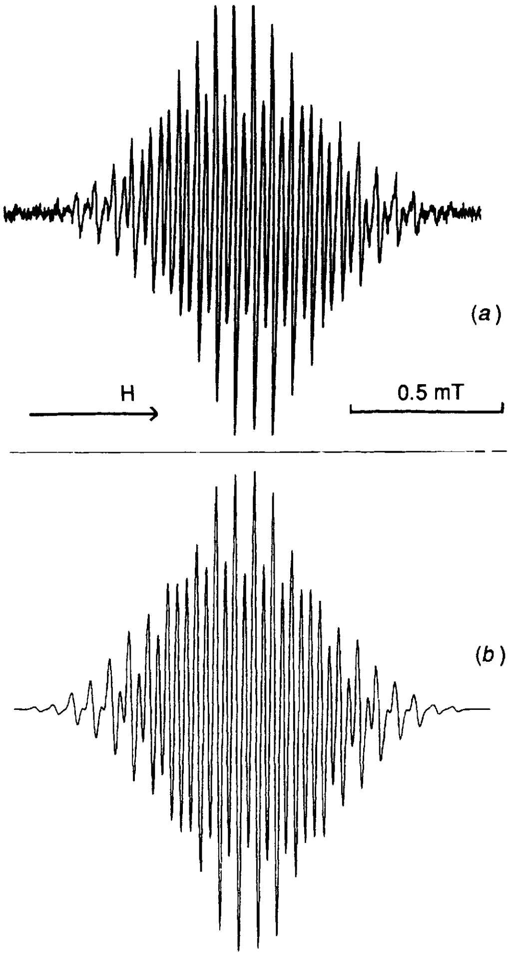


Fig. 2 EPR Spectrum of **5i** (*a*) and its simulation (*b*) computed with the data given in Table 1

Table 2 EPR data of fluorenyl radicals **12a–d** and the related radicals **1c,d**. Solvent: Ph_2O

Radical	*a* (H)/mT	*g*	*T*/K
12a[5]	R (3 H): 0.070; 1,3,6,8: 0.360 2,7: 0.091; 3,6: 0.360	—	383
12b	R (1 H): 0.043; 1,3,6,8: 0.336 2,7: 0.085; 4,5: 0.043	2.0035	463
12c	R (3 H): 0.025; 1,3,6,8: 0.343 2,7: 0.093; 4,5: 0.051	2.0030	453
12d[27]	1,8: 0.398; 2,7: 0.091 3,6: 0.376; 4,5: 0.064; R (1 H): 1.39	2.0025	233
1c[5]	R (1 H): 0.098; *o*: 0.250 *m*: 0.110; *p*: 0.275	2.0040	373
1d[5]	R (3 H): 0.070; *o*: 0.250 *m*: 0.110; *p*: 0.269	2.0037	373

for phenyl ($E^S_C = 0.39$).[24] The EPR spectrum of **5l** is a multiplet (10 lines or more) with a splitting of 0.063 mT. It is presumably caused by two protons of the indanedionyl system as in **5a**, **e**, **h**, **i**, **j** and by the *tert*-butyl protons which might show similar or slightly less splittings than the *tert*-butyl protons in the neopentyl radical ($a = 0.100$ mT).[25] The high *g* value of 2.0045 again indicates a high spin density at the carbonyl groups which is a consequence of the missing mesomeric interaction of *tert*-butyl with the indanedionyl system.

The 9-acylfluorenyls **12b**, **c** represent the 'fixed planar conformation' of the diarylmethyls **1c**, **d** discussed above. They have been generated from the corresponding dimers **13b**, **c** and these from 9-R,9-Hal-fluorenes **11**, see Scheme 3. The difluorenyls **13b**, **c** are known,[26] but their structure has so far been assigned without experimental evidence.

The radicals **12b**, **c** recombine, like the unsubstituted fluorenyl radical **12d**[26d] and **12a**,[5] exclusively by C–C coupling, giving **13b**, **c**. We have established this by ^1H NMR spectroscopy, see Experimental section. In no case has an enol type dimer been found, in contrast with the corresponding diphenylacylmethyl radicals **1c–e** which recombine by C–O coupling.[5] In Table 2, the EPR data of **12b**, **c** are listed. The assignments were made by analogy to the data for **12a**[5] and **12d**[27] which are included in the Table. The *g* values are somewhat smaller (by 0.0005–0.0007) than those of the unbridged radicals **1c**, **d** indicating a slightly enhanced steric strain at the trigonal carbon atom which lowers the mixing of the carboxy form to the radical state. Nevertheless, C–C dimerization has been found for **12b**, **c** showing that there are other than steric reasons which determine the structure of the dimers.

Experimental

The methods for working with air- and moisture-sensitive compounds have been described in former publications[1,5,6] and references given therein. Instrumental equipment: EPR, Varian E-109E; ENDOR, ER 200D with resonator EN 801; NMR [$(CH_3)_4Si$ as internal standard] Varian EM 360 A (60 MHz, ^1H) and Bruker AM 300 (300 MHz); IR, Perkin-Elmer 477 and 577; UV, Philips Unicam SP 1900; GC, Carlo-Erba 4160; Elemental analyses, Carlo-Erba 1106.

EPR and ENDOR measurements of **5** and **12** were performed by heating a solution of the dimers **6** or **10** under dry argon in the spectrometer. For details, see ref. 9.

2,2'-Diphenyl[*2,2'-biindane*]*-1,1',2,2'-tetrone* **6a**.—The title compound was synthesized according to the literature[13] in 76.2% yield (lit., 91%); m.p. 213 °C (lit., 213–214 °C); ν_{max}(KBr)/cm^{-1} 1700 (C=O), no ν(=C–O–C) at 1050–1070 or 1210–1250; δ_H($CDCl_3$) 7.3 (s, 10 H, ArH) and 7.6–8.2 (m, 8 H, indane).

2,2'-Di(1-naphthyl)[*2,2'-biindane*]*-1,1',2,2'-tetrone* **6b**.—2-(1-Naphthyl)indane-1,3-dione **9b** (4.1 g, 15 mmol)[12] and iodine (1.9 g, 7.5 mmol) were heated for 12 h in a solution of sodium ethoxide [prepared from sodium (0.4 g, 16 mmol) and ethanol (45 cm^3)]. After evaporating off the ethanol (20 cm^3) and cooling to -20 °C yellow crystals were obtained, washed three times with 0.1 mol dm^{-3} aqueous sodium thiosulfate and water, and recrystallized from ethanol–benzene (1 : 1); yield 2.8 g, 69%; m.p. 235 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1711 (C=O), 761 (2-subst. indane), no ν(=C–O–C); δ_H($CDCl_3$) 6.5–8.0 (m, ArH); δ_C($CDCl_3$) 70.97 [$(CO)_2C$-Naph], 123.89–136.20 ($C_{ar}H$, C_{ar}), 140.60 [$(CO)C_{ar}$] and 197.79 (CO) (Found: C, 84.5; H, 3.9. $C_{38}H_{22}O_4$ requires C, 84.12; H, 4.09%).

2-(9-Anthryl)indane-1,3-dione **9c**.—A solution of sodium methoxide [prepared from sodium (5.3 g, 230 mmol) and anhydrous methanol (75 cm^3)] was added to a stirred solution of **8** (6.7 g, 50 mmol) and **7c** (10.3 g, 50 mmol) in ethyl acetate (60 cm^3). The mixture was refluxed for 2 h. After removing the solvents the yellow solid residue was dissolved in water and acidified with concentrated hydrochloric acid. The remaining solid was filtered off and recrystallized from butan-2-one; yield 12.8 g, 79%; m.p. 220 °C; ν_{max}(KBr)/cm^{-1} 1169 (C=O) and 766 (2-subst. indane); δ_H($CDCl_3$) 7.1–7.8 (m, 18 H, ArH) and 7.9–8.2 (m, 8 H, indane) (Found: C, 85.7; H, 4.3. $C_{23}H_{14}O_2$ requires C, 85.70; H, 4.38%).

2,2′-*Di*(9-*anthryl*)[2,2′-*biindane*]-1,1′,2,2′-*tetrone* **6c**.—Compound **9c** (8.2 g, 40 mmol) and iodine (1.3 g, 5 mmol) were added to aqueous sodium ethoxide [produced from sodium (2.4 g, 10 mmol) and anhydrous ethanol (30 cm^3)]. After refluxing for 12 h and cooling, a yellow solid was separated and washed several times with 0.1 mol dm^{-3} aqueous sodium thiosulfate and water; yield 1.9 g, 59%; m.p. 240 °C (decomp.) [from ethanol–benzene (1 : 1)]; ν_{max}(KBr)/cm^{-1} 1684 (C=O) and 775 (2-subst. indane), no ν(=C–O–C); $\delta_H(CDCl_3)$ 7.1–7.8 (m, 18 H, ArH) and 7.9–8.2 (m, 8 H, indane); $\delta_C(CDCl_3)$ 56.63 $[(CO)_2CC)]$, 122.94–139.08 (HC_{ar}, C_{ar}), 141.27 $[(CO)C_{ar}]$ and 189.26 (CO) (Found: C, 86.2; H, 4.2. $C_{46}H_{26}O_4$ (624.7) requires C, 85.97; H, 4.08%).

2-(4-tert-*Butylphenyl*)*indane*-1,3-*dione* **9d**.—3-(4-*tert*-Butylbenzylidene)phthalide (4.0 g, 15 mmol) resolved in methanol (50 cm^3) was dropped into methanolate [prepared from sodium (0.50 g, 22 mmol) and anhydrous methanol (10 cm^3)]. After work-up of the dark red solution, crystals of **9d** were isolated; yield 57%; m.p. 131 °C; ν_{max}(KBr)/cm^{-1} 1740 (C=O); $\delta_H(CDCl_3)$ 1.3 (s, 9 H, Bu^t), 4.1 [s, 1 H, $(CO)_2CHAr$], 7–7.5 (m, 4 H, ArH) and 7.7–8.1 (m, 4 H, indane); $\delta_C(CDCl_3)$ 59.44 $[(CO_2)_2CHAr]$, 123.69–135.63 (HC_{ar}, C_{ar}), 142.63 $[(CO)C_{ar}]$, 150.65 $[(CH_3)_3CC_{ar}]$, 198.46 (CO), 34.51 $[(CH_3)_3C]$ and 31.25 $[(CH_3)_3C]$.

2,2′-*Di*(4-tert-*butylphenyl*)[2,2′-*biindane*]-1,1′,2,2′-*tetrone* **6d**.—Compound **9d** (1.0 g, 1.8 mmol) and iodine (0.23 g, 1.8 mmol) were added to ethanolate [prepared from sodium (0.05 g, 2 mmol) and dry ethanol (20 cm^3)]. The mixture was refluxed for 16 h, and ethanol (*ca.* 10 cm^3) was distilled off. After cooling, the title compound **6d** crystallized out, was washed with 0.1 mol dm^{-3} aqueous sodium thiosulfate (20 cm^3), water (20 cm^3) and some methanol, and was dried at 20 °C/12 Torr; yield 0.56 g, 56%; m.p. 232 °C; ν_{max}(KBr)/cm^{-1} 1740 (C=O), no ν(=C–O–C); $\delta_H(CDCl_3)$ 1.3 (s, 18 H, Bu^t), 7.1–7.5 (m, 8 H, ArH) and 7.7–8.2 (m, 8 H, indane); $\delta_C(CDCl_3)$ 64.23 $[(CO)_2CC]$, 123.64–135.41 (HC_{ar}, C_{ar}), 141.00 $[(CO)C_{ar}]$, 151.45 $[(CH_3)_3CC_{ar}]$, 197.56 (CO), 34.47 $[(CH_3)_3C]$ and 31.26 $[(CH_3)_3C]$.

2-(4-*Cyanophenyl*)*indane*-1,3-*dione* **9e**.—The title compound was prepared as described above for **9c** from equimolar amounts of 4-cyanobenzaldehyde and phthalide; yield 31%; m.p. 250 °C (decomp.); ν_{max}(KBr)/cm^{-1} 2220 (CN).

2,2′-*Di*(4-*cyanophenyl*)[2,2′-*biindane*]-1,1′,2,2′-*tetrone* **6e**.—Iodine (1.00 g, 8.0 mmol), resolved in 50% aqueous potassium iodide (25 cm^3), was dropped into a mixture of **9e** (1.00 g, 4 mmol) and potassium carbonate (1.00 g, 7 mmol) in water (70 cm^3), and then stirred for 1 h at 25 °C. Compound **6e** was deposited, filtered off, washed with water several times, and recrystallized from ethanol; yield 0.46 g, 47%; m.p. 255 °C (decomp.); ν_{max}(KBr)/cm^{-1} 2230 (CN) and 1740 (C=O); $\delta_H(CDCl_3)$ 7.3–7.9 (m, 8 H, ArH) and 8.0 (s, 8 H, indane); $\delta_C(CDCl_3)$ 63.56 $[(CO)_2CC]$, 124.02–136.33 (HC_{ar}, C_{ar}), 140.65 $[(CO)C_{ar}]$, 113.03 (CNC_{ar}), 196.17 (CO) and 118.11 (CN).

2-[4-(N,N-*Dimethylamino*)*phenyl*]*indane*-1,3-*dione* **9f**.—The title compound was prepared following ref. 14; yield 69%; m.p. 184 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1700 (C=O) and 772 (1,2-disubst. indane); $\delta_H(CDCl_3)$ 2.9 (s, 6 H, Me), 4.1 [s, 1 H, $(CO)_2CHAr$], 6.5–7.1 (m, 4 H, ArH) and 7.6–8.1 (m, 4 H, indane); $\delta_C(CDCl_3)$ 40.38 $[N(CH_3)_2]$, 59.06 $[(CO)_2CHAr]$, 112.86–135.65 (HC_{ar}, C_{ar}), 142.54 $[(CO)C_{ar}]$, 150.01 $[(CH_3)NC_{ar}]$ and 198.95 (CO).

2,2′-*Di*[4-(N,N-*dimethylamino*)*phenyl*][2,2′-*biindane*]-1,1′,2,2′-*tetrone* **6f**.—The title compound was prepared from **9f** (3.8 g, 15 mmol) in 2 mol dm^{-3} aqueous sodium hydroxide (20 cm^3), $K_3[Fe(CN)_6]$ (4.9 g, 15 mmol) in water (15 cm^3) and methylene dichloride (20 cm^3) following ref. 14, giving a yellow powder; yield 3.0 g, 79%; m.p. 213 °C (lit., 214 °C); ν_{max}(KBr)/cm^{-1} 1695 (C=O), no ν(=C–O–C); $\delta_H(CDCl_3)$ 2.9 (s, 12 H, Me), 6.5–7.1 (m, 8 H, ArH) and 7.5–8.0 (m, 8 H, indane); $\delta_C(CDCl_3)$ 40.12 $[N(CH_3)_2]$, 64.04 $[(CO)_2CHAr]$, 111.05–135.11 (HC_{ar}, C_{ar}), 140.96 $[(CO)C_{ar}]$, 150.17 $[(CH_3)NC_{ar}]$ and 198.76 (CO).

2,2′-*Di*(2-*chlorophenyl*)[2,2′-*biindane*]-1,1′,2,2′-*tetrone* **6g**.—Iodine (4.0 g, 32 mmol) in 50% aqueous KI (100 cm^3) was dropped into **9g** (3.0 g)[12] which was resolved in water (200 cm^3). This mixture was stirred for 1 h at 25 °C. The insoluble crystalline product was filtered off, washed with water, and twice precipitated slowly from chloroform by ethanol; yield 2.41 g, 81%; m.p. 183 °C; ν_{max}(KBr)/cm^{-1} 1745 (C=O), no ν(=C–O–C). $\delta_H(CDCl_3)$ 7.2–7.5 (m, 8 H, ArH) and 7.8–8.2 (m, 8 H, indane).

2-(2,4-*Xylyl*)*indane*-1,3-*dione* **9h**.—The title compound was prepared as described for **9c**. Yellow crystals; yield 79%; m.p. 132 °C (ethanol); ν_{max}(KBr)/cm^{-1} 1708 (C=O) and 769 (1,2-subst. indane); $\delta_H(CDCl_3)$ 1.3 (s, 6 H, CH_3), 4.5 [s, 1 H, $(CO)_2CHAr$], 6.6–7.3 (m, 3 H, ArH) and 7.8–8.2 (m, 4 H, indane); $\delta_C(CDCl_3)$ 20.12, 20.92 $(ArCH_3)$, 58.63 $[(CO)_2ArCH]$, 123.36–137.60 (HC_{ar}, C_{ar}), 142.23 $[(CO)_2C_{ar}]$ and 198.72 (CO) (Found: C, 81.7; H, 5.8. $C_{17}H_{14}O_2$ requires C, 81.58; H, 5.64%).

2,2′-*Di*(2,4-*xylyl*)[2,2′-*biindane*]-1,1′,2,2′-*tetrone* **6h**.—The title compound was obtained as a crystalline white solid according to the preparation of **10d**; yield 81%; m.p. 212 °C (ethanol); ν_{max}(KBr)/cm^{-1} 1708 (C=O) and 769 (1,2-subst. indane); $\delta_H(CDCl_3)$ 2.0–2.5 (2 s, 12 H, CH_3), 6.6–7.1 (m, 6 H, ArH) and 7.5–8.1 (m, 8 H, indane); $\delta_C(CDCl_3)$ 20.65 (CH_3), 68.98 $[(CO)_2C]$ and 123.44–142.08 (HC_{ar}, C_{ar}) (Found: C, 81.9; H, 5.0. $C_{34}H_{26}O_4$ requires C, 81.91; H, 5.26%).

2-(2,6-*Xylyl*)*indane*-1,3-*dione* **9i**.—The title compound was synthesized as described above for **9c**; yield 29%; m.p. 183 °C; ν_{max}(KBr)/cm^{-1} 1678 (C=O) and 762 (1,2-subst. indane); $\delta_H(CDCl_3)$ 1.9 (s, 3 H, CH_3), 2.4 (s, 3 H, CH_3), 4.8 [s, 1 H, $(CO)_2ArCH$], 6.9–7.2 (m, 3 H, ArH) and 7.8–8.1 (m, 4 H, indane); $\delta_C(CDCl_3)$ 21.23 $(ArCH_3)$, 58.49 $[(CO)_2ArCH]$, 123.25–138.85 (HC_{ar}, C_{ar}), 141.41 $[(CO)C_{ar}]$ and 198.56 (CO) (Found: C, 81.3; H, 5.8. $C_{17}H_{14}O_2$ requires C, 81.58; H, 5.64%).

1,3-*Dioxo*-2-(2,6-*xylyl*)*indan*-2-*yl* 3-*Oxo*-2-(2,6-*xylyl*)-3H-*inden*-1-*yl Ether* **10a**.—The title compound was prepared as described below for **10d**. The solid product was recrystallized from anhydrous ethanol in an argon atmosphere; yield 71%; m.p. 151 °C; ν_{max}(KBr)/cm^{-1} 1714 (C=O), 1249, 1066 (=C–O–C) and 763 (1,2-subst. indane); $\delta_H(CDCl_3)$ 2.0 (s, 6 H, CH_3), 2.4 (s, 6 H, CH_3) and 6.5–7.9 (m, 14 aromatic H); $\delta_C(CDCl_3)$ 20.89, 23.77, 24.24 $(ArCH_3)$, 88.53 $[(CO)_2C(O)Ar]$, 118.38–142.06 [HC_{ar}, C_{ar}], 131.19 [C(CO)ArC=C], 170.11 [Ar(O)C=C], 198.31 and 198.63 (CO) (Found: C, 82.2; H, 5.2. $C_{34}H_{26}O_4$ requires C, 81.91; H, 5.26%).

2-*Mesitylindane*-1,3-*dione* **9j**.—Following the synthesis described for **9c**; **9j** was obtained as a yellow powder; 74% yield; m.p. 215 °C (ethanol); ν_{max}(KBr)/cm^{-1} 1713 (C=O) and 765 (1,2-subst. indane); $\delta_H(CDCl_3)$ 0.9 (s, 3 H, CH_3), 2.3 (s, 3 H, CH_3), 2.5 (s, 3 H, CH_3), 4.8 [s, 1 H, $(CO)_2ArCH$], 6.7–7.1 (m, 2 H, ArH) and 7.8–8.1 (m, 4 H, indane); $\delta_C(CDCl_3)$ 20.89, 21.12 (CH_3), 58.28 $[(CO)_2ArCH]$, 123.22–138.66 (HC_{ar}, C_{ar}), 141.43 $[(CO)C_{ar})]$ and 198.8 (CO) (Found: C, 82.0; H, 6.1. $C_{18}H_{16}O_2$ requires C, 81.79; H, 6.10%).

2-*Mesityl*-1,3-*dioxoindan*-2-*yl* 2-*Mesityl*-3-*oxo*-3H-*inden*-1-

yl Ether **10b**.—The yellow solid was synthesized as described below for **10d** and recrystallized from anhydrous ethanol in an argon atmosphere; 55.8% yield: m.p. 158 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1708 (C=O), 1245, 1070 (=C–O–C) and 763 (1,2-subst. indane); δ_H(CDCl$_3$) 1.9–2.5 (m, 18 H, CH$_3$), 6.3 (s, 2 H, ArH), 6.9 (s, 2 H, ArH), 7.0–7.7 (m, 4 H, indane) and 7.8 (s, 4 H, indane); δ_C(CDCl$_3$) 20.52, 20.84, 24.02 (Ar*C*H$_3$), 88.77 [(CO)$_2$*C*(O)Ar], 116.04–141.49 (HC$_{ar}$, C$_{ar}$), 131.00 [(CO)-Ar*C*=C], 169.55 [Ar(O)*C*=C), 192.26 and 194.10 (CO) (Found: C, 82.4; H, 5.8. $C_{36}H_{30}O_4$ requires C, 82.11; H, 5.74%).

2-(2,4,6-*Triisopropylphenyl*)*indane*-1,3-*dione* **9k**.—The title compound was prepared as described for **9c**; yield 31%; m.p. 170 °C (methanol); ν_{max}(KBr)/cm^{-1} 1678 (C=O) and 772 (1,2-subst. indane); δ_H(CDCl$_3$) 0.7–1.4 (m, 18 H, CH$_3$) and 2.6–3.1 [m, 4 H, C*H*(CH$_3$)$_2$]; δ_C(CDCl$_3$) 23.91, 24.04, 24.31 [CH(*C*H$_3$)$_2$], 31.32, 34.40 [*C*H(CH$_3$)$_2$], 50.71 [(CO)$_2$Ar*C*H], 110.75–138.68 (HC$_{ar}$, C$_{ar}$), 149.55, 149.61 [(CO)*C*$_{ar}$] and 194.55 (CO) (Found: C, 82.7; H, 7.7. $C_{24}H_{28}O_2$ requires C, 82.73; H, 8.09%).

2-(2,4,6-*Triisopropylphenyl*)-1,3-*dioxoindan*-2-*yl* 3-*Oxo*-2-(2,4,6-*triisopropylphenyl*)-3H-*inden*-1-*yl Ether* **10c**.—Following the synthesis described below for **10d**; the orange, crystalline product was recrystallized from anhydrous ethanol; yield 55%; m.p. 95 °C; ν_{max}(KBr)/cm^{-1} 1710 (C=O), 1210 and 1053 (=C–O–C); δ_H(CDCl$_3$) 0.8–1.5 [m, 36 H, CH(C*H*$_3$)$_2$], 1.5–3.1 [m, 6 H, C*H*(CH$_3$)$_2$], 6.9–7.5 (m, 4 H, ArH) and 7.9–8.2 (m, 8 H, indane); δ_C(CDCl$_3$) 23.47, 24.04, [CH(*C*H$_3$)$_2$], 30.31–34.5 [*C*H(CH$_3$)$_2$], 89.84 [(CO$_2$)*C*(O)Ar], 116.36–151.05 (HC$_{ar}$, C$_{ar}$), 198.81, 199.94 and 201.81 (CO) (Found: C, 82.4; H, 7.9. $C_{48}H_{54}O_4$ requires C, 82.96; H, 7.83%).

2-tert-*Butylindane*-1,3-*dione* **9l**.—Using the method described for the preparation of **9c**, a yellow, viscous oil was isolated, which was purified by Kugelrohr distillation; 38% yield; b.p. (0.1 Torr) 92–93 °C; ν_{max}(KBr)/cm^{-1} 1708 (C=O) and 755 (1,2-subst. indane); δ_H(CDCl$_3$) 1.0 (s, 9 H, C(CH$_3$)$_3$], 2.6 [s, 1 H, (CO)$_2$CHBu^t] and 7.8 (m, 4 H, indane); δ_C(CDCl$_3$) 27.90 [C(*C*H$_3$)$_3$], 35.57 [*C*(CH$_3$)$_3$], 61.41 [(CO)$_2$*C*HBu^t], 122.17, 135.04 [HC$_{ar}$], 142.54 [(CO)*C*$_{ar}$] and 200.16 (CO) (Found: C, 77.5; H, 7.1. $C_{13}H_{14}O_2$ requires C, 77.20; H, 6.98%).

2-tert-*Butyl*-1,3-*dioxoindan*-2-*yl* 2-tert-*Butyl*-3-*oxo*-3H-*inden*-1-*yl Ether* **10d**.—K$_3$[Fe(CN)$_6$] (12.3 g, 37 mmol) dissolved in water was added to a solution of **9l** (3.0 g, 15 mmol) in 2 mol dm^{-3} sodium hydroxide (50 cm^3) and methylene chloride (50 cm^3) and stirred for 12 h at room temperature. The organic layer was washed several times with 0.1 mol dm^{-3} sodium hydroxide solution first, then with water and was dried over magnesium sulfate. After removing the solvents a highly viscous oil remained which was crystallized by stirring with hexane; yield 2.6 g, 85%; m.p. 199 °C; ν_{max}(KBr)/cm^{-1} 1694 (C=O), 1263, 1074 (=C–O–C) and 760 (1,2-subst. indane); δ_H(CDCl$_3$) 1.2 [s, 9 H, C(CH$_3$)$_3$], 1.6 [s, 9 H, C(CH$_3$)$_3$] and 6.2–7.9 (m, 8 H, ArH); δ_C(CDCl$_3$) 20.40, 29.92 [C(*C*H$_3$)$_3$], 32.49, 40.14 [*C*(CH$_3$)$_3$], 90.16 [(Bu^t)*C*–O], 119.08–140.98 (HC$_{ar}$, C$_{ar}$), 170.25 (Ar(O)*C*=C) and 196.66 (CO) (Found: C, 77.6; H, 6.4. $C_{26}H_{26}O_4$ requires C, 77.59; H, 6.51%).

9,9′-*Diformyl*-9,9′-*bifluorenyl* **13b**.—The title compound was prepared according to the literature;[28] yield 54%; m.p. 218 °C (lit., 218 °C); ν_{max}(KBr)/cm^{-1} 1740 (C=O); δ_H(C$_6$D$_6$) 5.8–6.65 (m, 16 H, fluorene) and 9.0 (s, 2 H, CHO) (Found: C, 87.1; H, 4.7. $C_{28}H_{18}O_2$ requires C, 87.05; H, 4.66%).

9,9′-*Diacetyl*-9,9′-*bifluorenyl* **13c**.—The title compound was prepared according to the literature;[28] yield 35%; m.p. 245 °C (lit., 242 °C); ν_{max}(KBr)/cm^{-1} 1710 (C=O); δ_H(CDCl$_3$) 0.9 (s, 6 H, CH$_3$) and 5.9–6.6 (m, 16 H, ArH) (Found: C, 87.0; H, 5.2. $C_{30}H_{22}O_2$ requires C, 86.85; H, 5.31%).

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