Liquid Chromatographic Optical Resolution of 2,2'-Spirobibenz[*e*]indan Derivatives and Absolute Stereochemistry as Determined by the C.D. Exciton Chirality Method

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2,2'-Spirobibenz[*e*]indan derivatives, (**1**) and (**2**), have been synthesized and optically resolved by means of liquid chromatography using a column with a chiral stationary phase of (+)-poly-(triphenylmethyl methacrylate); the absolute stereochemistry of each enantiomer was unambiguously determined by the c.d. exciton chirality method.

The c.d. exciton chirality method,[1] a powerful chiroptical tool for the determination of absolute stereochemistry of organic compounds, has been extensively applied to various natural products and synthetic chiral compounds including spirans.[2,3] Of the latter, spirobibenzindans[4] are particularly suitable for studying the intramolecular chiral exciton interaction by means of circular dichroism, since the exciton interaction between the ^1B_b transitions of two naphthalene chromophores is very effective. Of this class, 2,2'-spirobibenz[*e*]indan was chosen for study, its two ^1B_b electric transition moments, which are along the long axes of the naphthalene chromophores, being ideally oriented in space for strong exciton chirality (Figures 1 and 2) to occur. Furthermore, the 2,2'-spirobibenz[*e*]indan system has no mechanism by which homoconjugation between two chromophores, *i.e.*, a spiroconjugation of the spirans, can occur. This is an additional advantage in obtaining an intense c.d. Cotton effect, because both homoconjugation and conjugation tend to diminish its intensity. With these factors in mind, it was expected that 2,2'-spirobibenz[*e*]indan would give rise to an extremely strong c.d. Cotton effect in the region of the ^1B_b transition around 230 nm; this expectation was satisfied. We report the c.d. properties and the determination of the absolute configuration of 2,2'-spirobibenz[*e*]indans, and also describe the liquid chromatographic optical resolution using a column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate).[5]

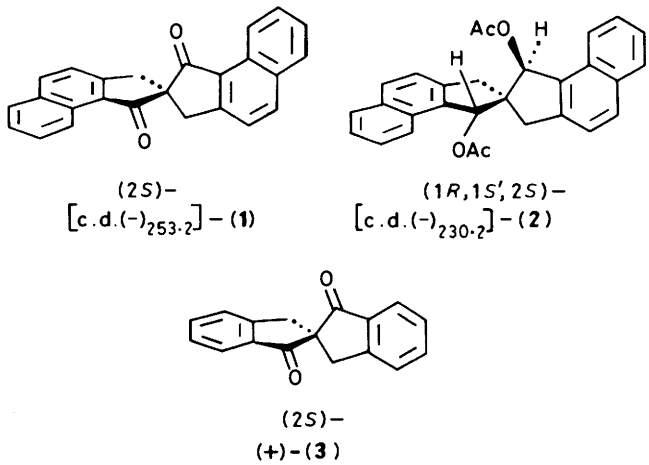


Figure 1. Absolute stereochemistry of the first-eluted enantiomers in the liquid chromatographic optical resolution using a column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate)

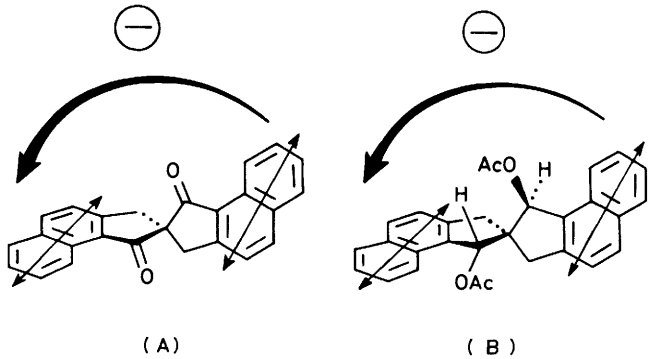
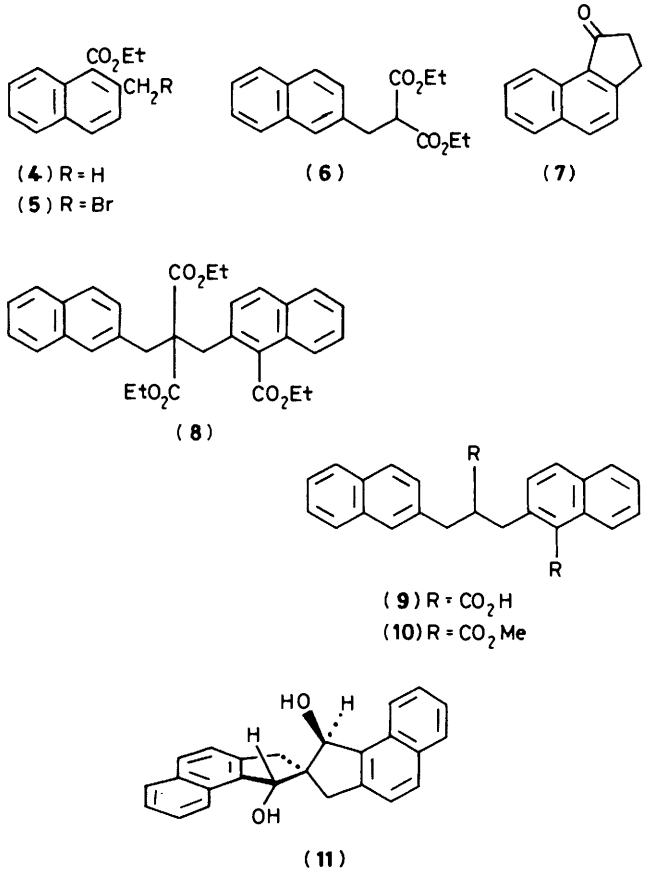


Figure 2. Negative exciton chirality between two ^1B_b transition moments in the system of (2*S*)-(**1**) (A) and (1*R*,1'*S*,2*S*)-(**2**) (B)

Results and Discussion

Synthesis of 2,2'-Spirobibenz[e]*indans.*—Racemic 1,1',3,3'-tetrahydro-2,2'-spirobi[2*H*-benz[*e*]indene]-1,1'-dione (**1**) was synthesized in a similar manner to 2,2'-spirobi-indan-1,1'-dione (**3**).[3] Ethyl 2-methylnaphthalene-1-carboxylate (**4**) was prepared from 1-bromo-2-methylnaphthalene[6] by a Grignard reaction with ethyl chloroformate. Although it is reported[7] that the anomalous Grignard reaction of 2-(bromomethyl)naphthalene with ethyl chloroformate gives the ester (**4**), the method was found to be impractical. Bromination of the ester (**4**) with *N*-bromosuccinimide (NBS) yielded the bromide (**5**) which decomposed on distillation. Therefore, the crude product was employed for the next reaction. The alkylation of diethyl (2-naphthylmethyl)propanedioate (**6**)[8,9] with the bromide (**5**) afforded the triester (**8**), which was subsequently hydrolysed and decarboxylated with KOH in DMSO–water to yield the dicarboxylic acid (**9**). Under the usual reaction conditions employing ethanol or ethylene glycol as solvents, the aromatic ester group remained unchanged. Compound (**9**) cyclized in the presence of polyphosphoric acid to give the desired diketone (**1**), the structure of which was confirmed on the basis of its ^1H n.m.r. spectrum which showed a single set of AB quartet peaks indicative of a C_2 symmetrical structure: δ 3.35 p.p.m. (2 H, d, *J* 17.2 Hz) and 3.90 (2 H, d, *J* 17.2 Hz). The diketone (**1**) was converted into the *cis,trans*-diacetate (**2**), the *cis,trans* configuration of which was confirmed by ^1H n.m.r.



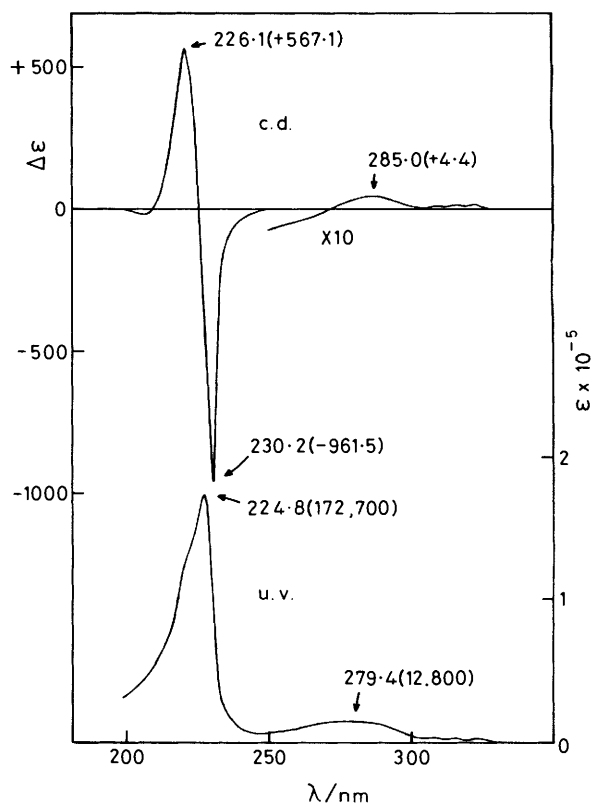


Figure 3. C.d. and u.v. spectra of (1*R*,1′*S*,2*S*)-[c.d.$(-)_{230.2}$]-(**2**) in ethanol

spectroscopy: δ 3.00 p.p.m. (1 H, d, *J* 17.2 Hz), 3.09 (1 H, d, *J* 17.2 Hz), 3.26 (1 H, d, *J* 17.2 Hz), and 3.64 (1 H, d, *J* 17.2 Hz). These data indicate a loss of C_2-symmetry in the structure of (**2**), and hence lead to the *cis,trans* configuration.

As a model compound representing half of the diketone (**1**), 2,3-dihydro-1*H*-benz[*e*]inden-1-one (**7**)[10] was prepared from the diester (**6**) in a similar manner to compound (**1**).

Liquid Chromatographic Optical Resolution.—All attempts to obtain optically active compounds (**1**) and (**2**), by the customary methods were unsuccessful. We thus adopted a direct chromatographic method for optical resolution, using a column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate);[5] this had been reported to be quite effective for optical resolution of compounds having aromatic groups. This method proved successful and both racemates (**1**) and (**2**) were optically resolved under a reverse-phase condition with methanol as eluant; resolution factors[11] (Rs) were 2.26 and 0.80 for (**1**) and (**2**), respectively. Each enantiomer thus obtained was purified by standard chromatography, in order to remove a contaminant of the chiral polymer.

The C.D. Spectra and Absolute Stereochemistry.—The c.d. spectrum of the first-eluted enantiomer of (**2**) was measured, using a sample of micrograms scale;* concentration of the solution used was determined from the u.v. absorbance. As expected, the c.d. spectrum exhibits typical exciton split Cotton effects of great intensity, $\lambda_{ext.}$ 230.2 nm, Δε −961.5 and $\lambda_{ext.}$ 221.6 nm, Δε +567.1, in the ^1B_b transition region, as shown in Figure 3. The amplitude ($A = \Delta\varepsilon_1 - \Delta\varepsilon_2$) of the present exciton split Cotton effects is A = −1 528.6, which is comparable with the largest value [for (6*R*,15*R*)-(+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene, A = +1 652.1] known for an organic compound.[1] Moreover, the A value of (**2**) is larger than those of any other spirobibenzindans[4] reported to date. The c.d. spectrum curve of the second-eluted enantiomer of (**2**) was clearly antipodal to that of the first-eluted enantiomer.

It is well established that the ^1B_b transition of a naphthalene chromophore is polarized along the long axis of the chromophore. Therefore, application of the c.d. exciton chirality method to the negative sign of the A value leads to the absolute stereochemistry, with a left-handed screw relationship between the long axes of two naphthalene chromphores, as shown in Figure 2. The (1*R*,1′*S*,2*S*) absolute configuration of the diacetate [c.d.$(-)_{230.2}$]-(**2**) † was thus determined in a non-empirical manner.

The c.d. spectrum of the first-eluted enantiomer of the diketone (**1**) also exhibits typical exciton split Cotton effects in the ^1B_b transiton region, as shown in Figure 4: $\lambda_{ext.}$ 253.2 nm, Δε −96.1 and $\lambda_{ext.}$ 214.0 nm, Δε +112.1. Since the A value (−208.2) is negative, the (2*S*) absolute configuration was unambiguously assigned to [c.d.$(-)_{253.2}$]-(**1**), as illustrated in Figure 2.

Unlike the case of the diacetate (**2**), the u.v. spectrum of the diketone (**1**) shows two absorption maxima in the ^1B_b transition (Figure 4): 236 nm (ε 46 800) and 212.8 nm (ε 80 300). One possible explanation of the phenomenon is to adopt the mechanism of u.v. exciton splitting due to the interaction

* A few runs of chromatographic optical resolution provide enough of the sample for c.d. measurements.

† In order to specify an enantiomer by c.d. data instead of optical rotation data, we propose a new prefix system; for example, [c.d.-$(-)_{230.2}$]-(**2**) indicates the enantiomer (**2**) showing a negative c.d. at 230.2 nm.

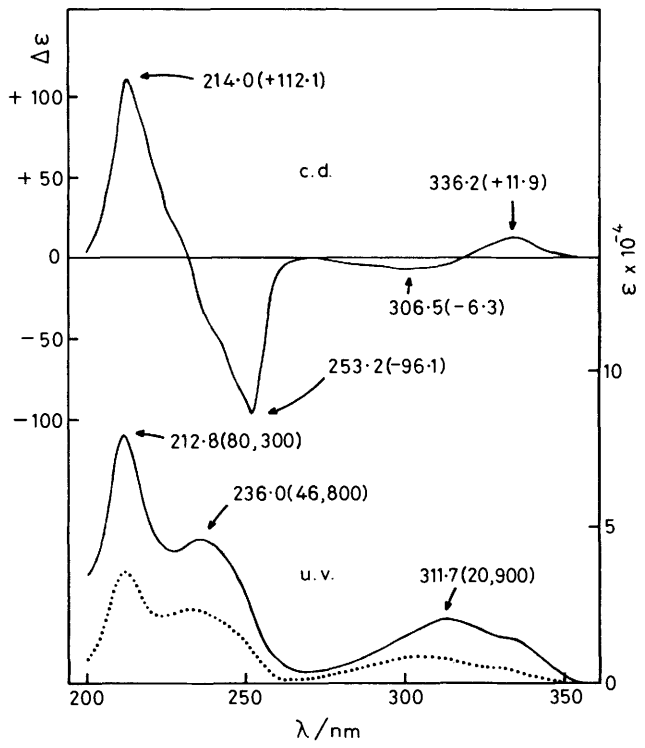


Figure 4. C.d. and u.v. spectra of (2*S*)-[c.d.$(-)_{253.2}$]-(**1**) in methanol. The dotted line shows the u.v. spectrum of (**7**) in ethanol

between two chromophores. However, this is not the case for (**1**) because the u.v. spectrum of 2,3-dihydro-1*H*-benz[*e*]inden-1-one (**7**), a model compound representing half of the diketone (**1**), also exhibits two maxima, as shown in Figure 4. From the u.v. data of (**7**), it is clear that the conjugation between the naphthalene and the carbonyl groups decreases the symmetry of the ^1B_b state, and hence the u.v. band of the ^1B_b transition splits into at least two bands. On the basis of the splitting, the whole shape of the ^1B_b band shows broadening, as shown in Figure 4.

The c.d. intensity of the diketone (**1**) is weaker than that of (**2**); this phenomenon can be explained by a decrease in the symmetry of the ^1B_b state. Thus, broadening of the u.v. band diminishes the intensity of the c.d. band, as observed in the case of bis(*p*-nitrobenzoates).[1] On the other hand, both of the u.v. and c.d. bands of the diacetate (**2**) are very sharp and strong. These results are instructive for application of the c.d. exciton chirality method; chromophores of high symmetry are much more suitable for the exciton method than those of low symmetry.

The first-eluted enantiomer [c.d.$(-)_{253.2}$]-(**1**) was reduced with $LiAlH_4$, followed by acetylation to give a *cis,trans*-diacetate, which was identical with the first-eluted enantiomer (1*R*,1′*S*,2*S*)-[c.d.$(-)_{230.2}$]-(**2**). Therefore, the (2*S*) absolute configuration of [c.d.$(-)_{253.2}$]-(**1**) was also confirmed by the chemical correlation.

Racemic 2,2′-spirobi-indan-1,1′-dione (**3**) was cleanly resolved by the same chromatographic method: Rs value 4.41. The first-eluted enantiomer was assigned as (2*S*)-(+)-(**3**), by comparison of the c.d. spectrum with that of the authentic sample.[3] The chromatographic behaviour of compounds (**1**), (**2**), and (**3**) indicates that the (2*S*) enantiomer is more rapidly eluted than the (2*R*) enantiomer. Thus, an enantiomer with two aromatic groups in a left-handed screw relationship interacts less with the chiral polymer than its enantiomer. This chromatographic behaviour is in line with the results of other cases previously reported.[5]

Experimental

Melting points were taken on a Yamato capillary melting point apparatus and are uncorrected. I.r. spectra were obtained as KBr discs, neat, or as solutions in $CHCl_3$ on a JASCO A-3 or a Hitachi EPI-G2 spectrophotometer. ^1H N.m.r. spectra were recorded on a JEOL PMX60, JEOL FX90Q (90 MHz, Fourier transform), or a JEOL JNMPS-100 spectrometer, with tetramethylsilane as internal standard. U.v. and c.d. spectra were obtained on a JASCO UVDEC-505 spectrophotometer and a JASCO J-400X spectropolarimeter, respectively. H.p.l.c. was performed on a Waters liquid chromatograph ALC/GPC-244. Mass spectra were recorded on a JEOL JMS-DX300 spectrometer. C.d. data ($\lambda_{ext.}$/nm, $\Delta\varepsilon$) are those of the extrema and zero-line intersections. Ether refers to diethyl ether.

Ethyl 2-Methylnaphthalene-1-carboxylate (**4**).—To a mixture of magnesium turnings (6.502 g, 267 mmol) and dry ether (30 ml) was added iodomethane (0.25 ml, 0.57 g, 4.02 mmol) under nitrogen. After reaction had begun, a solution of 1-bromo-2-methylnaphthalene[6] (10.0 g, 45 mmol) in dry ether (30 ml) was added dropwise. The mixture was gently refluxed for 1 h, during which time a white pasty cake appeared. The solid material was dissolved by adding dry benzene (33 ml) and then the mixture was refluxed for an additional 30 min. The reaction mixture was cooled to 0 °C and a solution of ethyl chloroformate (15 ml, 17.03 g, 157 mmol) in dry ether (20 ml) was added dropwise with ice-cooling. The mixture was refluxed for 5 h and then treated with a minimum amount of water to precipitate hydroxides. The organic layer was distilled under reduced pressure to give the ethyl ester (**4**) (6.584 g, 55%) as a yellow oil, b.p. 134—135 °C/1.0 mmHg; $\nu_{max.}$(neat) 2 960, 1 720, and 1 505 cm^{-1}; δ (60 MHz, CCl_4) 1.37 (3 H, t, *J* 7.2 Hz), 2.44 (3 H, s), 4.43 (2 H, q, *J* 7.2 Hz), and 7.25—7.97 (6 H, m); *m/z* 214.099 88 (M^+, 65%; $C_{14}H_{14}O_2$ requires 214.099 364).

Ethyl 2-(Bromomethyl)naphthalene-1-carboxylate (**5**).—A mixture of the ester (**4**) (32.2 g, 150 mmol), *N*-bromosuccinimide (34.71 g, 195 mmol), benzoyl peroxide (0.341 g, 1.41 mmol), and carbon tetrachloride (500 ml) was refluxed and illuminated with a sunlamp for 3 h, during which time a white precipitate deposited. The precipitate was filtered off and the organic layer was evaporated under reduced pressure to afford the crude bromide (**5**) (44.0 g, 100%); δ (60 MHz, CCl_4) 1.47 (3 H, t, *J* 7.8 Hz), 4.50 (2 H, q, *J* 7.8 Hz), 4.63 (2 H, s), and 7.3—8.0 (6 H, m). Since the bromide (**5**) was unstable, the crude product was used without further purification for the next reaction.

Diethyl 2-(1-Ethoxycarbonyl-2-naphthylmethyl)-2-(2-naphthylmethyl)propane-1,3-dioate (**8**).—Sodium metal (7.20 g, 176 mmol) was dissolved in dry ethanol (300 ml) under nitrogen. A solution of ethyl 2-(2-naphthylmethyl)propane-1,3-dioate (**6**)[8,9] (43.01 g, 147 mmol) in dry ethanol (410 ml) was added dropwise, and then a solution of the bromide (**5**) (44.06 g, 147 mmol) in dry ethanol (60 ml) and dry ether (315 ml) was added dropwise. After being refluxed for 2 h, the reaction mixture was poured into ice–water, and extracted with ether. The organic layer was washed with brine and evaporated to dryness. The residue was subjected to column chromatography on silica gel ($CHCl_3$), to yield the *triester* (**8**) (28.49 g, 39%); $\nu_{max.}$(neat) 1 720, 1 600, and 1 510 cm^{-1}; δ (100 MHz, CCl_4) 0.96 (6 H, t, *J* 8.0 Hz), 1.40 (3 H, t, *J* 7.2 Hz), 3.36 (2 H, s), 3.56 (2 H, s), 3.95 (4 H, q, *J* 8.0 Hz), 4.40 (2 H, q, *J* 7.2 Hz), and 7.2—7.9 (13 H, m); *m/z* 512.218 26 (M^+, 37%; $C_{32}H_{32}O_6$ requires 512.219 852).

2-(1-Carboxy-2-naphthylmethyl)-3-(2-naphthyl)propionic Acid (**9**).—A mixture of the triester (**8**) (13.3 g, 26 mmol), dimethyl sulphoxide (500 ml), KOH (14.17 g, 252 mmol), and water (120 ml) was stirred at 90 °C for 1.5 h. After being cooled to room temperature, the mixture was acidified to pH 1 with

30% aqueous HCl, and extracted with ether. The organic layer was washed with water and brine, and evaporated under reduced pressure to give the diacid (**9**) as a yellow solid (9.35 g, 94%); $\nu_{max.}$($CHCl_3$) 3 050, 1 705, 1 600, 1 510, 1 285, 1 150, and 1 110 cm^{-1}. A portion of the product (**9**) was esterified with diazomethane to yield the dimethyl ester (**10**); δ (100 MHz, $CDCl_3$) 2.76—3.45 (5 H, m), 3.46 (3 H, s), 3.81 (3 H, s), and 7.2—8.0 (13 H, m).

1,1′,3,3′-*Tetrahydro*-2,2′-*spirobi*[2H-*benz*[e]*indene*]-1,1′-*dione* (**1**).—A mixture of the diacid (**9**) (9.695 g, 25.2 mmol) and polyphosphoric acid [prepared by heating P_2O_5 (300 g) with 85% H_3PO_4 (300 ml)] was stirred at 140 °C for 3.5 h to give a black mixture which was poured into ice–water, and extracted with $CHCl_3$ (×4). The combined organic layers were washed with water, aqueous $NaHCO_3$, and brine, and then evaporated to dryness. The residue was subjected to a short column chromatography on silica gel ($CHCl_3$) to give a white solid. The product was further purified by recrystallization from chloroform to afford the *diketone* (**1**) (2.688 g, 31%), m.p. 285 °C (decomp.); $\nu_{max.}$(KBr) 3 050, 2 950, 1 680, 1 575, 1 515, 1 440, 1 305, 1 175, 1 085, and 760 cm^{-1}; δ (100 MHz, $CDCl_3$) 3.34 (2 H, d, *J* 17.5 Hz), 3.86 (2 H, d, *J* 17.5 Hz), 7.4—7.7 (6 H, m), 7.85 (2 H, br d, *J* 7.7 Hz), 8.05 (2 H, d, *J* 9.0 Hz), and 8.90 (2 H, br d, *J* 8.5 Hz); *m/z* 348.114 61 (M^+, 100%; $C_{25}H_{16}O_2$ requires 348.115 012).

(cis,trans)-1,1′,3,3′-*Tetrahydro*-2,2′-*spirobi*[2H-*benz*[e]*indene*]-1,1′-*diol* (**11**).—To a suspension of $LiAlH_4$ (0.131 g, 3.44 mmol) in dry THF (35 ml) was added dropwise a solution of the diketone (**1**) (0.300 g, 0.861 mmol) in dry tetrahydrofuran (40 ml) under nitrogen. After being gently refluxed for 2 h, the reaction mixture was quenched with wet ether and ethyl acetate, and treated with a minimum amount of water to precipitate hydroxides. The organic layer was evaporated to dryness to yield the *diol* (**11**) as white crystals (0.303 g, 100%), m.p. 186—195 °C (decomp.); $\nu_{max.}$(KBr) 3 540, 3 380, 2 930, 1 630, 1 590, 1 515, 1 170, 1 005, 815, and 750 cm^{-1}; δ (90 MHz Fourier transform, $CDCl_3$) 1.70 (2 H, br s), 2.90 (1 H, d, *J* 16.8 Hz), 2.98 (2 H, br s), 3.94 (1 H, d, *J* 16.8 Hz), 5.31 (1 H, s), 6.16 (1 H, s), 7.4—8.1 (10 H, m), and 8.47 (2 H, br d, *J* 9.3 Hz); *m/z* 352.144 34 (M^+, 1%; $C_{25}H_{20}O_2$ requires 352.146 308).

(cis,trans)-1,1′,3,3′-*Tetrahydro*-2,2′-*spirobi*[2H-*benz*[e]*indene*]-1,1′-*diyl Diacetate* (**2**).—To a solution of the glycol (**11**) (0.095 g, 0.270 mmol) in benzene (1.1 ml) and pyridine (0.48 ml, 6.10 mmol) was added acetic anhydride (0.33 ml, 3.56 mmol). After 21 h at room temperature the reaction mixture was poured into ice–water and extracted with ethyl acetate. The organic layer was washed with aqueous $CuSO_4$, water, and brine, and evaporated to dryness. The white crystals obtained were purified by preparative t.l.c. on silica gel ($CHCl_3$) and recrystallized from ethanol to yield the *diacetate* (**2**) (0.090 g, 76%), m.p. 211—213 °C; $\nu_{max.}$($CHCl_3$) 3 020, 1 730, 1 635, 1 595, 1 375, 1 240, 1 025, and 975 cm^{-1}; δ (100 MHz, $CDCl_3$) 1.92 (3 H, s), 2.08 (3 H, s), 3.00 (1 H, d, *J* 17.2 Hz), 3.09 (1 H, d, *J* 17.2 Hz), 3.26 (1 H, d, *J* 17.2 Hz), 3.64 (1 H, d, *J* 17.2 Hz), 6.40 (1 H, s), 7.06 (1 H, s), and 7.3—9.2 (12 H, m); *m/z* 436.167 76 (M^+, 63%; $C_{29}H_{24}O_4$ requires 436.167 432).

General Procedure for Chromatographic Optical Resolution.—A column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate)[5] was mounted in a h.p.l.c. apparatus, cooled at 15 °C, and equilibrated with methanol as eluant. The samples were injected as acetonitrile solutions. Separation of enantiomers was monitored by a u.v. detector. Since a small amount of the polymer of the chiral stationary phase was present as a contaminant, the fraction of each enantiomer resolved was purified by preparative t.l.c. on silica gel ($CHCl_3$).

(2S)-1,1′,3,3′-*Tetrahydro*-2,2′-*spirobi*[2H-*benz*[e]*indene*]-1,1′-*dione* (**1**).—The c.d.$(-)_{253.2}$ enantiomer was obtained as the first-eluted fraction on h.p.l.c.; $\lambda_{max.}$(MeOH) 311.7 (ε 20 900), 236.0 (46 800), and 212.8 nm (80 300); $\lambda_{ext.}$(MeOH) 336.2 (Δε +11.9), 306.5 (−6.3), 253.2 (−96.1), and 214.0 nm (+112.1). A second-eluted fraction yielded the (2*R*)-[c.d.$(+)_{253.2}$] enantiomer, the c.d. spectrum of which was antipodal to that of (2*S*)-(**1**). The resolution factor Rs of the two peaks was 2.26.

(1R,1′S,2S)-1,1′,3,3′-*Tetrahydro*-2,2′-*spirobi*[2H-*benz*[e]*indene*]-1,1′-*diyl Diacetate* (**2**).—(a) The (1*R*,1′*S*,2*S*)-[c.d.$(-)_{230.2}$] enantiomer was obtained as first-eluted fraction on h.p.l.c.; $\lambda_{max.}$(EtOH) 279.4 (ε 12 800) and 228.4 nm (172 700); $\lambda_{ext.}$(EtOH) 285.0 (Δε +4.4), 230.2 (−961.5), and 221.6 nm (+567.1). A second-eluted fraction gave (1*S*,1′*R*,2*R*)-[c.d.$(+)_{230.2}$]-(**2**). The resolution factor Rs was 0.80. (b) The diketone (2*S*)-[c.d.$(-)_{253.2}$]-(**1**) obtained by the h.p.l.c. was reduced with $LiAlH_4$ to the glycol (1*R*,1′*S*,2*S*)-(**11**), as in the case of racemic (**1**). The glycol obtained was then converted into the diacetate (1*R*,1′*S*,2*S*)-[c.d.$(-)_{230.2}$]-(**2**), which was identical with the enantiomer directly obtained by h.p.l.c.

2,3-*Dihydro*-1H-*benz*[e]*indene*-1-*one* (**7**).—Naphthalene-2-propanoic acid prepared from the diester (**6**) was cyclized in the same manner as for compound (**9**) to give the ketone (**7**) (34%), m.p. 101.0 °C (from light petroleum) (lit.,[9] 102.3—103.8 °C; lit.,[10] 105.2—106.6 °C); $\nu_{max.}$($CHCl_3$) 3 020, 1 695, 1 630, 1 575, 1 510, 1 445, 1 310, 1 175, 1 110, and 840 cm^{-1}; δ (100 MHz, $CDCl_3$) 2.74 (2 H, m), 3.15 (2 H, m), 7.4—8.1 (5 H, m), and 9.16 (1 H, br d, *J* 8.5 Hz); $\lambda_{max.}$(EtOH) 329.3 (ε 5 000), 304.8 (9 000), 232.5 (23 800), and 213.2 nm (35 300); *m/z* 182.073 57 (M^+, 100; $C_{13}H_{10}O$ requires 182.073 154).

Acknowledgements

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