In conclusion some general remarks are in order. We have argued that configuration interaction has profound effects on chemical reactivity. The condition for maximum configuration interaction is that there exists a diexcited configuration of similar energy to the lowest state configuration of the transition state complex or molecule. This criterion has been consistently utilized in our discussions. However, it should be pointed out that the matrix element between the lowest state and diexcited configurations should also be greater than zero and appreciable in magnitude for configuration mixing to be strong. Fortunately, this condition is almost always met, since the crucial matrix element reduces to an exchange integral which, for some appropriate geometry of the transition state complex or of the molecule, is usually significantly greater than zero. Many configuration interaction calculations of ground state and excited molecules can be cited in support of this argument. One should also be cautioned against semantic pitfalls. A pericyclic transition state complex can be either symmetrical or unsymmetrical. In all likelihood, most pericyclic transition states are unsymmetrical in nature since asymmetry lifts the prohibition to extensive configuration mixing which is otherwise imposed by symmetry itself. Thus, a pericyclic transition state can resemble a singlet dipolar or diradical species, but can never be equated to them since such entities do not exhibit bonding along the polar or radical termini, by definition. Finally, it is important to single out people who have expressed related ideas with respect to the importance of configuration interaction. In this respect, the important contributions of Bader,[8] Salem,[9] and Pearson[10] merit our attention. More recently, the effect of configuration interaction on specific organic reactions has been discussed in interesting papers by Buenker and Peyerimhoff[11] and Trindle.[12] Finally, an interesting paper on concertedness has recently been contributed by Schmidt.[13]

Acknowledgment. I wish to express my appreciation to Professor P. v. R. Schleyer for his helpful comments and interest in this work. I am indebted to Professor L. Salem for his critical comments. Professor C. Trindle kindly made available some of his work prior to publication and Professor R. C. Cookson informed us of similar ideas regarding the problem of sigmatropic reactions. Finally, discussions with Professor J. A. Berson and comments of Professor P. D. Bartlett are gratefully acknowledged. The author is pleased to acknowledge the support of the Petroleum Research Fund (Grant 2653-G1) and the Research Corporation.

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Absolute Configuration and Chiroptical Properties of Optically Active 1,1′-Spirobiindan, 1,1′-Spirobiindene, and 1,1′-Spirobiindanone[1]

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Abstract: (*R*)-(+)- and (*S*)-(−)-1,1′-spirobiindan, (*S*)-(−)-1,1′-spirobiindene, and (*S*)-(+)-1,1′-spirobiindan-3-one and the related *R*-(+) monoolefin and *R*-(−) monoketone have been prepared in a state of high enantiomeric purity. Their configurations, as assigned by Horeau's method, concur with those assigned independently by others. The long-wavelength rotations can be accounted for by coupling (B-mode) of major local polarizability axes, in a simple form of the helical conductor model. The ultraviolet Cotton effects are discussed in terms of sector rules and various coupled oscillator models of optical activity.

Chiral substances with C_2 symmetry (one twofold rotation axis) are of interest because their chiroptical properties ([M]D, ORD, and CD) may reveal the ways in which the chromophores interact with one another under the influence of light.[2] For example, 1,1′-spirobiindan (**5**, Chart I) contains two phenyl groups that could interact with light (a) essentially independently, (b) cooperatively as a composite chromophore *via* diphenylmethane homoconjugation (π transmission), (c) as oscillators coupled through dipole–dipole interactions (through-space transmission), or (d) as parts of a framework in which a collection of electrons suffers small, but concerted and cooperative, displacements along bonds (σ transmission). In the first case, the Cotton effects would correspond in location to those of suitably analogous mononuclear indans and be about twice as large. In the second case a Cotton effect not seen in monoindans would appear, potentially quite strong and with a sign corresponding to the chirality of the composite chromophore.[3] In the third case, as

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(1) (a) A Useful Model of Optical Activity. X. (b) Part IX: J. H. Brewster and R. S. Jones, Jr., *J. Org. Chem.*, 34, 354 (1969).

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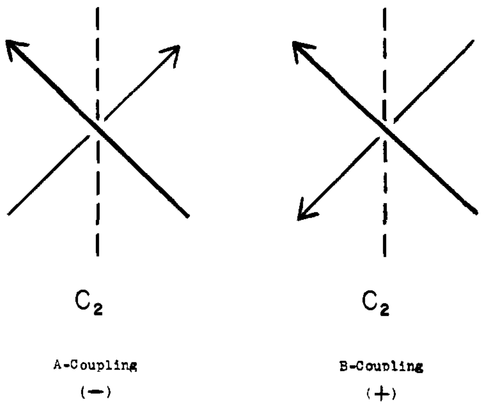

Figure 1. Modes of coupling of transition moments or polarizability axes in substances with C_2 symmetry.

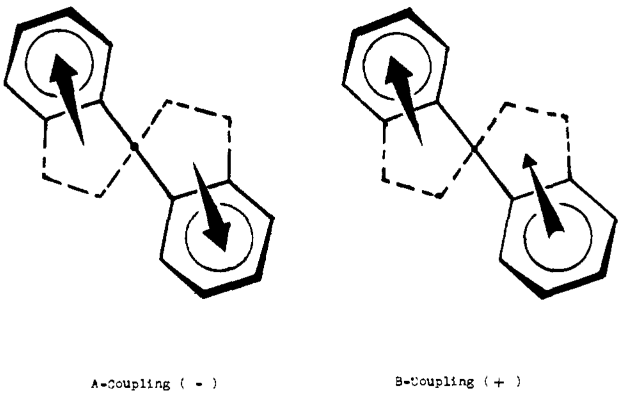

Figure 2. Coupling of long-axis transition moments or axes of polarizability in (*R*)-1,1′-spirobiindan. The C_2 axis is perpendicular to the plane of the paper at the spiro atom.

Mason has shown in many related cases,[4–8] the absorption band would be split into two components, corresponding to symmetrical (A) and antisymmetrical (B) modes of coupling of the transition moments (Figure 1), with Cotton effects of opposite sign. If the two modes are energetically different, they will occur at different wavelengths and, so, not cancel, but both appear in the region of the absorption band. For the case shown in Figure 1, A-coupling has the character of a left-handed helix (negative chirality) and would produce a negative Cotton effect[2,4–8] and levorotation at long wavelengths,[9] while B-coupling (positive chirality) would produce a positive Cotton effect and dextrorotation. The mode of coupling that is energetically favored, by whatever mechanism, be it σ or π transmission or dipole–dipole interactions through space, will be the one responsible for the longer wavelength Cotton effect.[2,4–8] Thus, as seen in the case of (*R*)-1,1′-spirobiindan (Figure 2), B-coupling of the long-axis transition moments would be energetically preferred over A-coupling (by any mechanism) and so would give rise to a positive Cotton effect on the long wavelength edge of an absorption band having this orientation of transition moment. Finally, the interaction of local axes of polarizability can be analyzed in terms of the helical conductor model of optical activity.[9] In the case given in Figure 2, the C_2 axis of each indan moiety should be one of the principal axes of polarizability and B-coupling of these axes with transmission of electrical effects through space or *via* σ bonds should be preferred. On this simple basis, (*R*)-1,1′-spirobiindan should be dextrorotatory at long wavelengths.

These principles, coupled with our interest in the chiroptical properties of indans[10,11] and styrenes,[12–14] as well as our interest in the determination of absolute configurations of spirans,[1b] have prompted us to prepare **5** and several of its derivatives in optically active form and to determine their absolute configurations by use of the method of Horeau.[15] We have since learned of the independent synthesis and rigorous chemical assignment of configuration to these same compounds by Hill.[16] In addition, an important series of tetramethyl-1,1′-spirobiindans has been prepared and assigned configuration *via* X-ray analysis.[17–19]

The preparation of both the *R* and *S* forms of 1,1′-spirobiindan (**5a,b**), the *S* forms of 1,1′-spirobiindene (**6**) and 1,1′-spirobiindanone (**4**), and the *R* forms of the corresponding monoolefin **9** and monoketone **8** is outlined in Chart I. The starting material, 3,3-diphenylglutaric anhydride (**1**), was prepared from benzophenone by stepwise condensation with acetonitrile,[20] hydrolysis, and treatment with acetic anhydride.[21] Methanolysis, cyclization by the method of Johnson and Glenn[22] (successive reaction with thionyl chloride and aluminum chloride), and saponification gave the racemic keto acid **3**. This was readily resolved with quinine. The racemic acid is lower melting (mp 129 *vs.* 166°) and more soluble than the active forms so that partially resolved material could be brought to optical purity by one or two crystallizations from chloroform–carbon tetrachloride. Cyclization[22] of the (+)-keto acid **3b** gave (+)-1,1′-spirobiindanone (**4**), reduced by the Clemmensen method[23] to (−)-1,1′-spirobiindan (**5b**). Reduction of the diketone with sodium borohydride gave a mixture of diastereomeric alcohols; gas chromatography on Fluoropak 80 at 150° gave a single product, (−)-1,1′-spirobiindene (**6**), which is notable for its large rotation ([M]D −1470). The (−)-keto acid **3a** was reduced[23] to (+)-1-carboxymethyl-1-phenylindan (**7**), and this was cyclized[22] to the (−)-monoketospirobiindan (**8**), from which the (+) monoolefin **9** and the dextrorotatory form of 1,1′-spirobiindan (**5a**) could be prepared by the methods used with the diketone.

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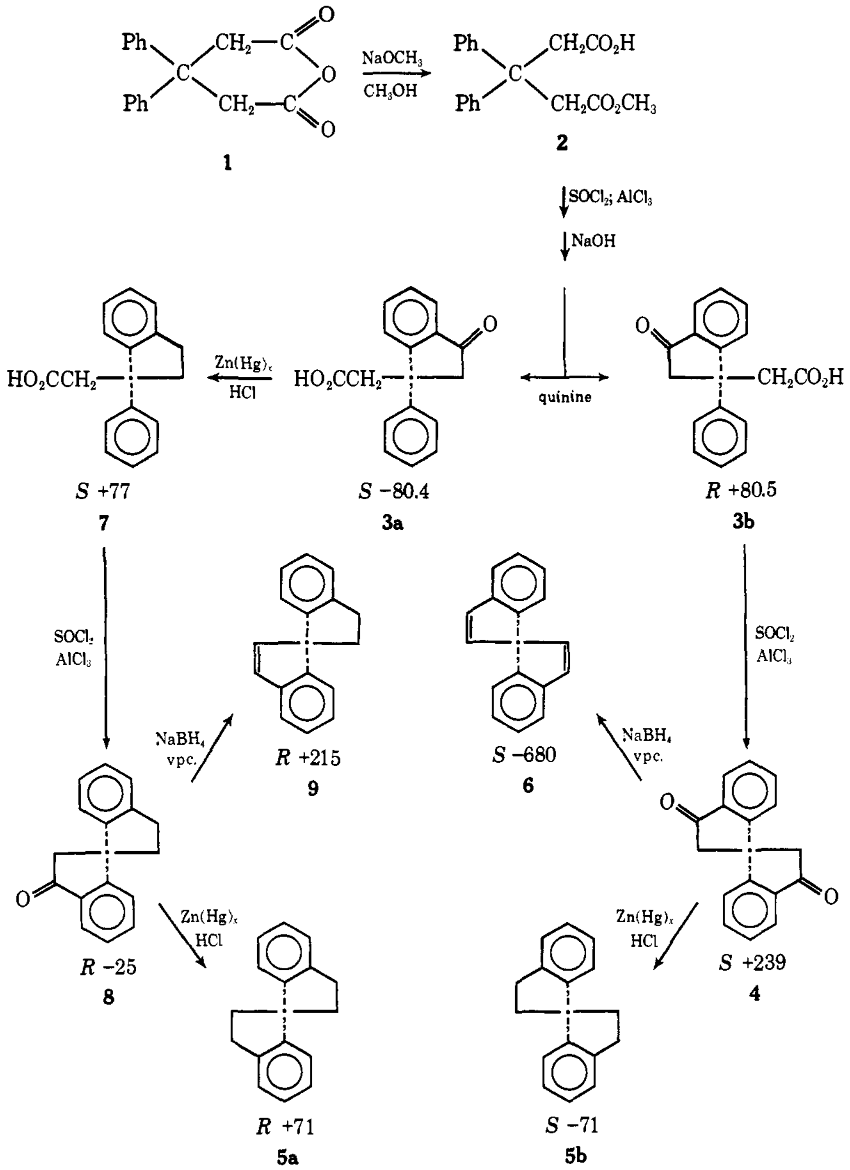
Chart I. Preparation of Optically Active 1,1′-Spirobiindan and Related Compounds[a]

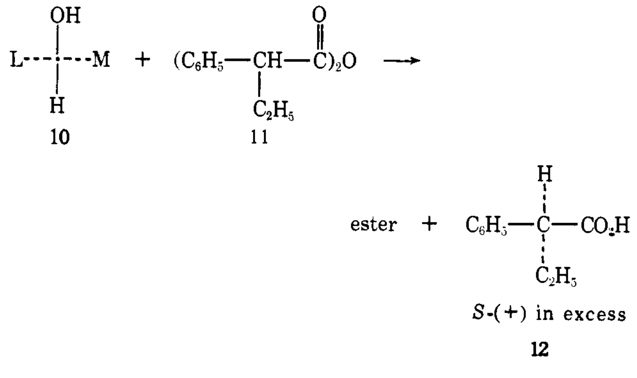


[a] Rotations shown as $[\alpha]_D$ in chloroform.

These assignments of structure are supported by ir, nmr, and mass spectral data.

We believe that the substances have been obtained essentially enantiomerically pure. Repeated recrystallization of quinine salt that gave (+)-**3b** with $[\alpha]_D$ +80.7° gave no increase in rotation, nor did repeated recrystallization of the keto acid itself, once this rotation was achieved. This conclusion was confirmed by use of the method of Raban and Mislow,[24,25] which depends on the principle that diastereomers may have different enough nmr spectra that the relative amounts of the two forms can be obtained by integration of particular peaks. Incompletely resolved (+)-**3b** ($[\alpha]_D$ +45.2°; calculated 0.779 mol fraction of (+) isomer on the basis that +80.7° is the rotation of the pure (+) enantiomer) was treated with thionyl chloride and then with (*S*)-(−)-α-methylbenzylamine of high optical purity ($[\alpha]^{24}_D$ −39.8°; lit.[26] $[\alpha]^{22}_D$ −40.3°) to give a mixture of the diastereomeric amides in 95% yield (whence little fractionation can have occurred). The nmr spectrum of this mixture ($CDCl_3$) contained two well-resolved methyl group doublets (*J* = 7 Hz) centered at τ 9.05 and 8.75; integration showed the mixture to contain 0.771 mol fraction of the diastereomer giving the latter signal and 0.229 of that giving the former, in adequate agreement with values obtained from rotation data (above).

Horeau[15] has shown that alcohols having the configuration **10** generally react with racemic α-phenyl-



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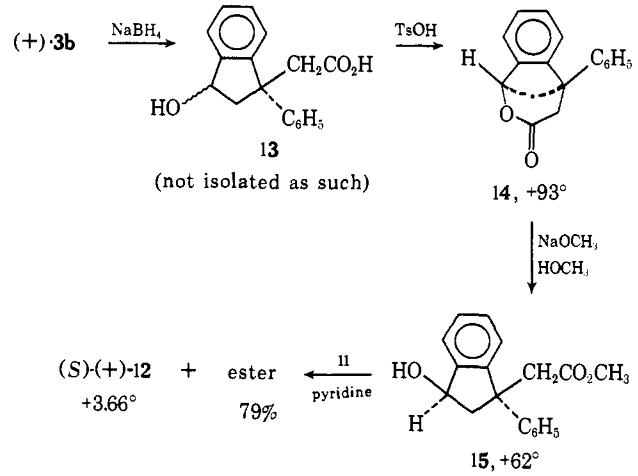
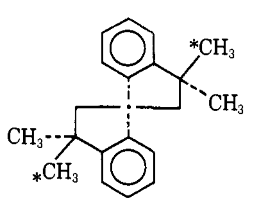
butyric anhydride (**11**) to give an excess of that diastereomeric form of the ester derived from the *R* acid, leaving acid containing an excess of the *S*-(+) form. This method appeared to be applicable in the present system since it had been shown to be successful with (*R*)[27]-(−)-1-indanol[28] (phenyl group large) and with ferrocene[29] and benchrotrene[30] derivatives of 1-indanol and 1-hydroxytetralin. The (+)-keto acid **3b** was reduced with sodium borohydride to a mixture of diastereomeric hydroxy acids (**13**, Chart II). Treatment with toluenesulfonic acid gave the lactone **14**; it is presumed that both hydroxy acids can give lactonization under conditions in which carbonium ions could be formed. The (+) lactone was cleaved quantitatively to the (−)-hydroxy ester **15** with sodium methoxide in methanol. Treatment with α-phenylbutyric anhydride in pyridine[15] gave 79% esterification and residual acid with $[\alpha]_D$ +3.66 ($CHCl_3$). This indicates that the carbinol center has the *R* configuration shown in **15** and, thus, that the other chiral center also has the *R* configuration as shown in **15**. The configurations[31] of the compounds shown in Chart I follow directly. It is to be recognized that remote groups may control the outcome of this method of assignment of configuration; cases have been reported where compounds epimeric at the carbinol center give the same enantiomer of residual acid.[32,33] There remains room for dispute on the applicability of such empirical methods.[34,35] It is, accordingly, gratifying that our results are in accord with those of Hill,[16] which rely on chemical degradation methods. In addition, the compounds of Hagishita, *et al.*,[17-19] have been interrelated among themselves, and one member has been assigned absolute configuration by the X-ray method. On this basis, their (−)-3,3,3′,3′-tetramethyl-1,1′-spirobiindan (**16**) and its (+)-5,5′-dimethyl homolog (**17**, X = CH_3) both have the *R* configuration. A comparison of the CD spectra shows conclusively that the aromatic rings have the same chiral disposition in space in **5a** as in **16** and **17** (Table I). All show a fine-structured positive Cotton effect with three clear maxima in the region 260–280 nm, attributable to the ^1L_b band. All show a negative Cotton effect at 225–231 nm and a stronger positive one at 216–223 nm (separation about 8 nm in each case), which Hagishita, *et al.*,[17-19] have attributed to a coupled splitting of the ^1L_a band. All give evidence of a strong positive Cotton effect at lower wavelengths which may be due to one of the B bands. This is a striking case where the long-wavelength rotations bear little relation to the Cotton effects observed in the accessible ultraviolet. Thus, our compound **5** in the *R* configuration has $[M]_D$ +156° while the 3,3,3′,3′-tetramethyl analog (which has only one small negative Cotton effect in this region) has $[M]_D$ −84°.

Chart II. Absolute Configurations by the Method of Horeau and Kagan[24,25]





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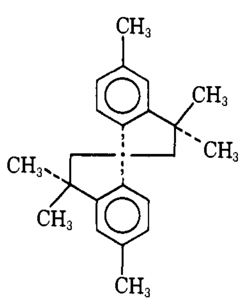

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Experimental Section[36]

3,3-Diphenylglutaric anhydride (1) was prepared by heating a solution of 3,3-diphenylglutaric acid in acetic anhydride to reflux:[21] mp 147–148° (lit.[21] mp 147–148°); nmr ($CDCl_3$) τ 6.52 (s, 4, methylene), 2.70 (s, 10, phenyl); ir ($CHCl_3$) 1821, 1773 (C=O stretch), 1076, 1064 cm^{-1} (C–O stretch).

Methyl hydrogen 3,3-diphenylglutarate (2) was prepared by the gradual addition of 3% methanolic sodium methoxide to a slurry of 22.0 g of 3,3-diphenylglutaric anhydride in 100 ml of methanol to a phenolphthalein end point. After 5 min, the clear solution was poured into 300 ml of 10% hydrochloric acid and extracted with dichloromethane. The extract was treated with carbon black, dried (Na_2SO_4), and filtered. The solvent was removed under reduced pressure and the residue was recrystallized from ether–pentane to yield 20.4 g (83%) of half ester: mp 127.8–128.0°; nmr ($CDCl_3$) τ 6.65 (s, 3, OCH_3), 6.50 (s, 2, $CH_2CO_2CH_3$), 6.45 (s, 2, CH_2CO_2H), 2.85 (s, 10 phenyl), 0.20 (s, 1, CO_2H); ir ($CHCl_3$) 3256–2410 (broad, O–H stretch), 1736, 1706 (C=O stretch), 1164 cm^{-1} (C–O stretch).

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.66; H, 5.94.

3-Carbomethoxymethyl-3-phenyl-1-indanone. The acid chloride of **2** was formed by reaction of 11.0 ml of thionyl chloride with 30.3 g of half ester (3 hr at 40°), excess thionyl chloride being removed by repeated codistillation with benzene. The acid chloride, in 10 ml of benzene, was added slowly to a slurry of 33.5 g of aluminum

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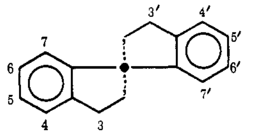
Table I. Chiroptical Properties of Symmetrically Substituted (*R*)-1,1′-Spirobiindans



Substituents (solvent)					Circular dichroism peaks λ, nm ([θ] × 10^{-3})			
3,3,3′,3′	5,5′	6,6′	7,7′	[M]D	$^{1}L_b(\alpha)$	$^{1}L_a(p)$	$^{1}B(\beta)$	Ref
H	H (MeOH)	H	H	+156	274 (+11.9) 268 (+7.5) 260 (+3.8)	225 (−42.5) 220^{d} (+10.2)	216^{d} (+31.1) 210 (+48.1)	*a*
H	OH (MeOH)	H	H	+117	289.5 (+19.2) 271.5 (−0.9)	232.5 (−30.7)		*b*
CH_3	H (isooctane)	H	H	−84	273 (+18.2) 267 (+10.3) 260 (+2.3) 253 (+1.3)	226 (−3.2) 221 (+33.7)	205^{f} (+14.8)	*c*
CH_3	CH_3 (isooctane)	H	H	+5.5	279 (+20.2) 273 (+10.4) 265 (+3.2)	231 (−13.3) 223 (+23.5)	216 (+45.5)	*c*
CH_3	CH_3 (MeOH)	OH	H	+64	292 (+17.6) 274 (−1.65)	231 (−15.8) 223^{e} (+14.6)	209 (+250)	*b*
CH_3	CH_3 (dioxane)	OH	Br	−540	293 (−5.25)	245 (−11.2) 231 (−5.18)	211 (+100)	*b*
CH_3	NH_2 (MeOH)	H	H	+26	297 (+15.7)	247 (−19.8) 230 (+9.1)	213 (−68.7) 204 (+125)	*c*
CH_3	$NH_3^+Cl^-$ (HCl–MeOH)	H	H		275 (+8.9) 268 (+6.8) 261 (+3.4)	236 (+1.1) 227 (−23.3)	200^{f} (+186)	*c*
CH_3	CO_2H (MeOH)	H	H	−194	286 (−4.0) 278 (−4.6)	250 (−33.0) 230^{d} (+34.8)	215 (+330)	*c*
CH_3	$CO_2^-Na^+$ (0.1 *N* NaOH)	H	H		284 (−3.2) 276 (−2.0)	248 (−30.6) 230^{d} (+28.2)	213 (+171)	*c*
CH_3	H (MeOH)	CH_2OH	H	+208	277 (+25.7) 271 (+12.4) 263 (+1.9)	228 (−37.1) 223 (+32.2)	210^{f} (+383)	*b*
CH_3	H (MeOH)	OH	H		290 (+10.9) 284 (+8.1) 270 (−2.0)	236 (+2.0) 229 (−18.6)	209 (+289)	*b*
CH_3	H (MeOH)	NH_2	H	+440	299 (+14.1)	244 (+25.7) 233 (−62.7)	220 (+607)	*b*
CH_3	H (HCl–MeOH)	$NH_3^+Cl^-$	H	+120	275 (+58.4) 269 (+35.3) 261 (+10.6) 247 (+5.1)	227 (−39.3) 221 (+82.2)	210^{f} (+266)	*b*
CH_3	H (MeOH)	CO_2H	H	+344	289 (+19.4) 283 (+7.8) 275 (−2.6)	249 (+95.0) 232 (−65.0)	217 (+337)	*b*
CH_8	H (0.1 *N* NaOH)	$CO_2^-Na^+$	H	+204	285 (+23.8) 277 (+13.3)	245 (+66.0) 232 (−64.7)	219 (+137)	*b*

[a] This work. [b] S. Hagishita, *et al.*, *Bull. Chem. Soc. Jap.*, **44**, 496 (1971). [c] S. Hagishita, *et al.*, *ibid.*, **44**, 2177 (1971). [d] Shoulder. [e] Inflection. [f] Final reading.

chloride in 100 ml of benzene, reaction temperature being kept below 10°. After 4 hr, 100 ml of ether was added and the reaction mixture was poured into a slurry of 1:1 ice–hydrochloric acid. The organic layer was extracted successively with 10% hydrochloric acid, 5% potassium hydroxide, and a saturated sodium chloride solution, dried ($CaSO_4$), and concentrated under reduced pressure; the residue was recrystallized from ether–pentane to yield 19.8 g (70.4%) of 3-carbomethoxymethyl-3-phenyl-1-indanone: mp 87.5–88.0°; nmr ($CDCl_3$) τ 6.55 (s, 3, methoxy), 6.78 (q, 2, J = 19 Hz, methylene), 6.72 (q, 2, J = 15 Hz, methylene), 2.97–2.10 (m, 9, phenyl); ir (KBr) 1715 (C=O stretch), 1170 cm^{-1} (C-O stretch).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.20; H, 5.77.

3-Carboxymethyl-3-phenyl-1-indanone (3). The ester (80.7 g) was hydrolyzed with a solution of 19.4 g of potassium hydroxide in 400 ml of methanol maintained at 25° for 72 hr. The methanol was removed at reduced pressure; the residue was acidified (10% HCl) and extracted with dichloromethane. The extract was dried ($CaSO_4$), concentrated at reduced pressure, and recrystallized from ether–pentane to yield 75.4 g (98.5%) of 3-carboxymethyl-3-phenyl-1-indanone: mp 128.5–129.0°; nmr ($CDCl_3$) τ 6.82 (q, 2, J = 20 Hz, methylene), 6.75 (q, 2, J = 16 Hz, methylene), 3.00–2.15 (m, 9, phenyl), 0.07 (s, 1, CO_2H); ir ($CHCl_3$) 3571–2410 (broad, O–H stretch), 1715 cm^{-1} (C=O stretch).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.60; H, 5.42.

Resolution of 3-Carboxymethyl-3-phenyl-1-indanone (3a and 3b). A solution of 6.1 g (18.8 mmol) of quinine in 150 ml of dry methyl ethyl ketone (MEK) was heated to reflux and treated with 5.0 g (18.8 mmol) of 3-carboxymethyl-3-phenyl-1-indanone. The salt which crystallized after 48 hr at 24° was collected, mp 187.5–192.0°, $[\alpha]^{25}D$ −79.8° (*c* 2.3396, $CHCl_3$). An ether suspension of 0.2 g of this salt was extracted with 10% hydrochloric acid. The ether solution was dried (Na_2SO_4) and concentrated under reduced pressure to yield 0.062 g of acid, mp 164.0–164.3°, $[\alpha]^{25}D$ +69.8° (*c* 0.6188, $CHCl_3$). The rest of the salt was repeatedly recrystallized from 75 ml of fresh MEK. While the melting point of the salt gradually rose to 196.0–196.5°, its specific rotation varied erratically between −70.9 and −87.1°. A portion of each crop of salt was cleaved and the acid recovered. After three recrystallizations of the salt, the melting point of the recovered acid had risen to 165.5–166.0° and the specific rotation had risen to +80.7° (*c* 1.3410, $CHCl_3$). After a total of eight recrystallizations, the salt

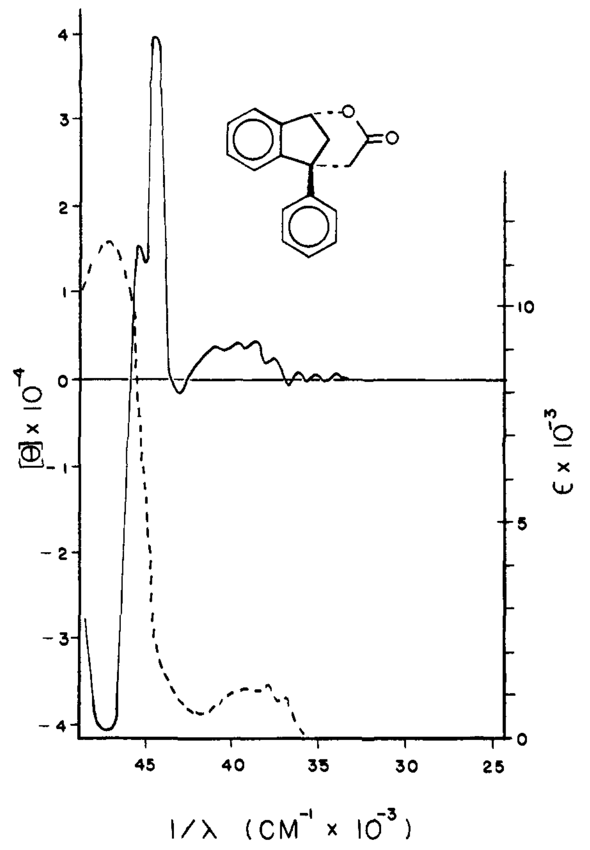


Figure 3. CD (—) and uv (- - -) spectra of (+)-3-(*R*)-carboxymethyl-3-phenyl-1-(*R*)-indanol lactone (**14**) in isooctane.

Table II. Principal Ultraviolet Maxima of Indan Derivatives

Compd (solvent)	${}^1L_b$	Band [λ, nm (ε × 10^{-3})] ${}^1L_a$ (aromatic)	Other groups
Indan[a] (isooctane)	273 (1.48) 267 (1.29) 260.5 (0.81) 259 (0.81)	216 (7.40) 211.5 (8.50)	
7 (MeOH)	271 (1.12) 264 (1.20) 259 (1.03)	214 (9.54)	
5 (MeOH)	272 (2.31) 265 (1.98) 259.5 (1.28) 253 (0.743)	{223 (7.23)}[d] {220 (7.67)} 213 (14.23)	
1-Indanone[b] (cyclohexane)	292 (2.50) 282 (2.50) 276 (2.00)		243 (15.8) 235 (20.0)
3 (MeOH)	291.5 (2.07)	209 (20.30)	243.5 (10.25)
8 (MeOH)	293 (2.46) 272 (2.23) 264.5 (1.95)	212 (19.39)	243.5 (9.95)
4 (MeOH)	292.5 (4.33) 288.5 (4.13)	211.5 (22.20)	242.5 (20.21)
Indene[c] (isooctane)		221 (10.7) <210	230–300: 250 (10.0)
9 (MeOH)		222[d] (26.10) 218 (30.10)	230–300: 272 (5.78) 265 (8.02) 258 (8.16)
6 (MeOH)		226 (26.30)	250–300: 297 (1.89) 285 (3.79) 274.5 (6.07) 266.5 (6.22)

[a] API Research Project 44 II, No. 400, 1950. [b] P. Ramart-Lucas and J. Hoch, *Bull. Soc. Chim. Fr.*, 19, 220 (1952). [c] API Research Project 44 II, No. 321, 1949. [d] Shoulder.

was cleaved and the resulting acid recrystallized from $CHCl_3$ to yield 1.07 g (21.4%) of (*R*)-(+)-3-carboxymethyl-3-phenyl-1-indanone (**3b**), mp 165.5–166.0°, $[\alpha]^{25}D$ +80.5° (*c* 0.6390, $CHCl_3$).

Subsequently, 23.3 g (87.6 mmol) of racemic acid and 28.4 g (87.6 mmol) of quinine were mixed in 600 ml of MEK which was heated at reflux. The crystals that formed after 48 hr were collected, cleaved, and recrystallized from $CHCl_3$–CCl_4 to yield 5.47 g (20.6 mmol, 23.4%) of acid, $[\alpha]^{26}D$ +79.8° (*c* 1.2886, $CHCl_3$) which rose to +80.7° after a single recrystallization of the partially resolved acid from $CHCl_3$–CCl_4. The crystalline salt which formed in the original mother liquor after a total of 6 days at 24° was similarly collected, cleaved, and recrystallized to yield 3.23 g (1.21 mmol, 13.9%) of (*S*)-(−)-3-carboxymethyl-3-phenyl-1-indanone (**3a**), $[\alpha]^{26}D$ −80.4° (*c* 1.1422, $CHCl_3$) which similarly rose to 80.7° after a single recrystallization. The ir and nmr spectra of (*R*)-(+)-3-carboxymethyl-3-phenyl-1-indanone were identical with those for racemic material. Uv, see Table II; $[\alpha]^{26}D$ +77.4° (*c* 0.6948, CH_3OH); ORD (*c* 1.92 × 10^{-3}, CH_3OH) [M] (nm) +970 (400), 0 (357), +20,620 (305), 0 (290), −8310 (277), −5540 (272.5), −7630 (296), −4850 (265), −6690 (262), −5960 (258), −5540 (252.5), −7070 (245), −47,100 (227), 0 (218), +37,380 (214), 0 (209); CD (*c* 1.92 × 10^{-3}, CH_3OH) [θ] (nm) 0 (400), −2830 (338), −5870 (327), 0 (310), +23,100 (295), +7400 (275), +9360 (270), +6310 (267), +9360 (263), +6970 (259), +12,390 (235), 0 (228), −54,400 (220), 0 (213), +40,900 (212).

(+)-3-(*R*)-Carboxymethyl-3-phenyl-1-(*R*)-indanol Lactone (14). A solution of 2.0 g of (*R*)-(+)-3-carboxymethyl-3-phenyl-1-indanone in 100 ml of ethanol was neutralized with 10% aqueous sodium hydroxide and treated with 0.40 g of sodium borohydride. After 24 hr at 26°, the solution was acidified with 5% hydrochloric acid and extracted with ether. The ether extract was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was taken up in 50 ml of benzene and heated at reflux for 20 hr with 0.05 g of *p*-toluenesulfonic acid. Water was removed with a Dean-Stark trap. The solution was extracted with saturated sodium bicarbonate and water, dried ($CaSO_4$), and concentrated under reduced pressure; the residue was crystallized from ether–pentane to yield 1.13 g (60%) of the lactone: mp 130.0–130.5° (racemic mp 92.0–92.5°); nmr ($CDCl_3$) τ 7.42 (q, 2, *J* = 13 Hz, $-CH_2CO_2-$), 6.83–6.70 (m, 2, $-CO_2CHCH_2-$), 4.37–4.25 (m, 1, $-CO_2CHCH_2-$), 3.20–2.98 (m, 1, ortho phenyl hydrogen), 2.65 (s, 8, phenyl); ir (melt) 1739 (C=O stretch), 1189 cm^{-1} (C–O stretch).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.87; H, 5.80.

Uv max (isooctane) 213 nm (ε 11,490), 251 (1012), 257 (1185), 263 (1208), 270 (956); $[\alpha]^{24}D$ +92.8° (*c* 0.6780, $CHCl_3$); ORD (*c* 1.841 × 10^{-3}, isooctane) [M] (nm) +406 (400), +1820 (297), +1479 (293), +1862 (288), +1563 (284), +2635 (278), +1498 (273), +4935 (271), +3425 (266), +4498 (263), +2038 (258), +2412 (256), 0 (243), −1767 (237), 0 (233), +19,271 (227), 0 (225), −40,250 (218), 0 (211); CD (*c* 1.841 × 10^{-3}, isooctane) [θ] (nm) 0 (400), +556 (295), +149 (290), +364 (286), 0 (281), +771 (276), 0 (274), −1113 (272), 0 (270), +2302 (267), +2141 (264), +4327 (260), +3747 (257), +4229 (254), +3533 (247), +3800 (244), 0 (235), −2195 (233), 0 (230), +39,631 (225), +13,382 (222), +15,544 (221), 0 (219), 40,146 (212), −27,299 (208). The CD and uv spectra of **14** are shown in Figure 3.

(−)-3-(*R*)-Carbomethoxymethyl-3-phenyl-1-(*R*)-indanol (15) was prepared by the gradual addition of 10 ml of 3% methanolic sodium methoxide to a solution of 0.123 g of (+)-3-(*R*)-carboxymethyl-3-phenyl-1-(*R*)-indanol lactone in 50 ml of methanol. After 45 min at 26°, the solution was poured into 200 ml of water and extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was recrystallized from pentane to yield 0.14 g (100%) of the alcohol: mp 47.5–48.0°; nmr (CCl_4) τ 7.50 (q, 2, *J* = 14 Hz, $-CHOHCH_2$), 6.97 (q, 2, *J* = 16 Hz, $-CH_2CO_2-$), 6.12 (s, 1, OH), 5.03 (t, 1, *J* = 6 Hz, $-CHOHCH_2-$), 6.73 (s, 3, OCH_3), 2.97 (s, 5, monosubstituted phenyl), 2.80 (s, 4, disubstituted phenyl); ir (melt) 3401 (O–H stretch), 1742 (C=O stretch), 1171 cm^{-1} broad (C–O stretch).

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.44; H, 6.50.

Uv max (CH_3OH) 211 nm (ε 12,020), 257 (609), 262.5 (701), 269.5 (607); $[\alpha]^{25}D$ −62.3° (*c* 1.4295, $CHCl_3$), $[\alpha]^{25}D$ −65.4° (*c* 0.6095, CH_3OH); ORD (*c* 3.072 × 10^{-3}, CH_3OH) [M] (nm) −516 (400), −839 (295), 0 (277), +203 (276), 0 (275), −2259 (271), −1186 (267), −2765 (264), −2039 (260), −2489 (256),

−2195 (253), −2305 (249), 0 (236), +1809 (230), 0 (228), −66,750 (220), 0 (213); CD (c 3.072 × 10^{-3}, CH_3OH) $[\theta]$ (nm) 0 (400), +2344 (272), +478 (269), +1650 (265), +232 (261), +521 (257), +90 (247), +24,963 (223), 0 (217), +20,260 (211), +9045 (205).

Application of Horeau's Method to the Determination of Absolute Configuration of 3-Carbomethoxymethyl-3-phenyl-1-indanol. To a solution of 0.3072 g (1.089 mmol) of levorotatory 3-carbomethoxymethyl-3-phenyl-1-indanol in 5 ml of anhydrous pyridine was added 3 ml of a pyridine solution of 0.7794 g (2.51 mmol) of racemic 2-phenylbutyric anhydride. After 20 hr at 28°, 1 ml each of water and benzene were added to the reaction. After 30 min the solution was titrated with 0.1012 *N* NaOH to a phenolphthalein end point. Since 41.12 ml of base was required for neutralization, esterification had proceeded to the extent of 79%. The basic solution was extracted with chloroform, acidified with dilute hydrochloric acid, and extracted with chloroform. This extract was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure to yield 0.651 g of (*S*)-(+)-2-phenylbutyric acid, $[\alpha]^{26}\mathrm{D}$ +3.66° (c 3.3214, $CHCl_3$), for an optical yield of 18.8%; ir[37] and nmr[38] spectra were identical with those published by Sadtler.

(*S*)-(+)-1-Carboxymethyl-1-phenylindan (7). Zinc amalgam was prepared from 24 g of 20 mesh zinc, 2 g of mercuric chloride, 1 ml of hydrochloric acid, and 20 ml of water; it was washed with 50 ml of water by decantation. There were then added 35 ml of hydrochloric acid, 15 ml of water, and a solution of 3.0 g of (*S*)-(−)-3-carboxymethyl-3-phenyl-1-indanone in 20 ml of toluene. This mixture was refluxed for 7 days with 5 ml of hydrochloric acid being added every 10 hr. The mixture was then poured onto ice and extracted with dichloromethane; the extract was dried (Na_2SO_4) and concentrated under reduced pressure and the residue was crystallized from ethanol–water to yield 2.16 g (76%) of the acid: mp 108.0–108.5°; nmr ($CDCl_3$) τ 7.67–6.70 (m, 6, methylene), 2.85 (s, 9, phenyl), −0.79 (s, 1, CO_2H); ir ($CHCl_3$) 3571–2427 (O-H stretch), 1721 cm^{-1} (C=O stretch).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.83; H, 6.63.

Uv, see Table II; $[\alpha]^{24}\mathrm{D}$ +77.2° (c 0.8032, $CHCl_3$), $[\alpha]^{24}\mathrm{D}$ +74.1° (c 0.7706, CH_3OH); ORD (c 2.303 × 10^{-3}, CH_3OH) [M] (nm) +342 (400), +1200 (290), +941 (285.7), +2570 (277), +1540 (269), +3260 (265), +2910 (261), +4620 (245), +3770 (235), +45,400 (221), +20,400 (215); CD (c 2.303 × 10^{-3}, CH_3OH) $[\theta]$ (nm) 0 (400), 0 (280), −2580 (275), −680 (270), −2070 (267), 0 (254), −13,990 (225), 0 (222), +50,900 (210).

(*R*)-(−)-3-Oxo-1,1′-spirobiindan (8). The acid chloride of (*S*)-(+)-**7** was obtained by treatment of 1.0 g of the acid with 0.43 ml of thionyl chloride in 10 ml of benzene at 40° for 3 hr, excess thionyl chloride and benzene being then removed under reduced pressure. The acid chloride was taken up in 10 ml of benzene and added to a slurry of 0.79 g of aluminum chloride in 50 ml of benzene with the reaction temperature being kept below 10°. After 3 hr the mixture was poured into 200 ml of 1:1 ice–hydrochloric acid and extracted with ether. The organic extract was washed with 10% hydrochloric acid, 5% potassium hydroxide, and a saturated sodium chloride solution, dried ($CaSO_4$), concentrated under reduced pressure, and distilled to yield 0.87 g (93%) of the spiran: bp 161–162° (0.5 mm); nmr ($CDCl_3$) τ 7.92–7.38 (m, 2, $PhCH_2CH_2$–), 7.15 (q, 2, J = 7 Hz, –$COCH_2$–), 6.88 (t, 2, J = 7 Hz, $PhCH_2CH_2$–), 3.37–1.80 (m, 8, phenyl); ir (neat) 1718 (C=O stretch), 754 cm^{-1} (ortho-disubstituted phenyl); mass spectrum (75 eV) m/e (rel intensity) 234 (100), 235 (19.3), 236 (2.38), 219 (31.0), 206 (16.9), 191 (14.5), 129 (14.5).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.39; H, 6.09.

Uv, see Table II; $[\alpha]^{27}\mathrm{D}$ −24.9° (c 0.5410, $CHCl_3$), $[\alpha]^{24}\mathrm{D}$ −45.6 (c 0.7304, CH_3OH); ORD (c 1.611 × 10^{-3}, CH_8OH) [M] (nm) −1450 (400), 0 (387), +2290 (350), 0 (340), −21,100 (306), 0 (290), +6640 (280), +1830 (274), +5490 (271), 0 (260), −3210 (249), 0 (242), +80,000 (220), +84,200 (216), +121,100 (212), 0 (206); CD (c 1.611 × 10^{-3}, CH_8OH) $[\theta]$ (nm) 0 (400), +8010 (327), 0 (288), −19,480 (281), −6890 (265), −9380 (262), −3590 (258), −6410 (255), −5280 (251), −16,310 (235), −21,100 (228), −43,400 (216), 0 (208), +32,100 (204).

(*R*)-(+)-2,3-Dihydro-1,1′-spirobiindene (9). A solution of 0.183 g of (*R*)-(−)-**8** in 20 ml of ethanol was treated with 0.25 g of sodium borohydride at 25°. After 30 min the solution was acidified with 10% hydrochloric acid and extracted with dichloromethane. The extract was dried ($CaSO_4$), concentrated under reduced pressure, and submitted to gas chromatography (10% FFAP on Fluoropack 80 at 125°) to yield 0.10 g (56%) of the monoolefin: nmr (CCl_4) τ 7.60 (t, 2, J = 7 Hz, $PhCH_2CH_2$–), 6.80 (t, 2, J = 7 Hz, $PhCH_2$-CH_2–), 3.47 (q, 2, J = 5 Hz, vinyl), 3.13–2.65 (m, 8, phenyl); ir (neat) 746 cm^{-1} (ortho-disubstituted phenyl); mass spectrum (75 eV) m/e (rel intensity) 218 (100), 219 (19.0), 220 (2.8), 217 (55.0), 216 (23.9), 215 (36.7), 203 (22.5), 202 (31.0).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.02; H, 6.69.

Uv, see Table II; $[\alpha]^{25}\mathrm{D}$ +215.0° (c 0.4160, $CHCl_3$), $[\alpha]^{25}\mathrm{D}$ +193.5° (c 0.4098, CH_3OH); ORD (c 2.055 × 10^{-3}, CH_3OH) [M] (nm) +1340 (400), +25,900 (279), +19,600 (273), +20,800 (270), 0 (261), −25,200 (248), −25,800 (241), −37,900 (231), 0 (225), +38,200 (222); CD (c 2.055 × 10^{-3}, CH_3OH) $[\theta]$ (nm) 0 (400), −2340 (296), 0 (290), −670 (287), 0 (285), +22,800 (274), +24,000 (272), +37,300 (264), +36,400 (262), +38,900 (260), +25,400 (250), 0 (238), −45,700 (224), 0 (213).

(*S*)-(+)-1,1′-Spirobi-3-indanone (4). The acid chloride obtained from the reaction of 1.25 ml of thionyl chloride and 3.0 g of (*R*)-(+)-3-carboxymethyl-3-phenyl-1-indanone was taken up in 10 ml of benzene and added to a slurry of 3.76 g of aluminum chloride in 30 ml of benzene so that the reaction temperature was kept below 10°. After 4 hr, the mixture was poured into 200 ml of 1:1 ice–hydrochloric acid and extracted with ether. The extract was washed successively with 10% hydrochloric acid, 5% potassium hydroxide, and saturated sodium chloride solution, dried ($CaSO_4$), and concentrated under reduced pressure; the residue was recrystallized from ethanol to yield 0.99 g (35%) of the spiran: mp 213.5–214.0°; nmr ($CDCl_3$) τ 6.88 (s, 4, methylene), 3.37–2.08 (m, 8, phenyl); ir ($CHCl_3$) 1789 cm^{-1} (C=O stretch); mass spectrum (70 eV) m/e (rel intensity) 248 (100), 249 (19.1), 250 (1.68), 247 (25.8), 192 (19.7), 193 (18.6), 189 (13.5), 180 (14.6).

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 81.89; H, 5.19.

Uv, see Table II; $[\alpha]^{24}\mathrm{D}$ +238.7° (c 0.6400, $CHCl_3$), $[\alpha]^{25}\mathrm{D}$ +233.5° (c 0.2158, CH_3OH); ORD (c 1.360 × 10^{-3}, CH_3OH) [M] (nm) +2020 (400), 0 (384), +4340 (333.3), +37,820 (298), 0 (283), −20,200 (273), 0 (259), +12,120 (250.5), 0 (239), −233,400 (216), −79,600 (210); CD (c 1,360 × 10^{-3}, CH_3OH) $[\theta]$ (nm) 0 (400), −2580 (355), −2870 (350), −8300 (342), −8300 (338), −12,310 (328), −11,180 (320), −11,420 (317), −6880 (310), 0 (306), +49,800 (286), +8202 (262), +90,000 (230), 0 (220), −230,000 (212), 0 (206).

(*S*)-(−)-1,1′-Spirobiindene (6). A solution of 0.20 g of (*S*)-(+)-**4** in 20 ml of ethanol was treated with 0.25 g of sodium borohydride at 25°. After 30 min the solution was acidified with 10% hydrochloric acid and extracted with dichloromethane. The extract was dried (Na_2SO_4), concentrated under reduced pressure, and submitted to gas chromatography (10% FFAP on Fluoropack 80 at 150°) to yield 0.096 g (55%) of the spiran: nmr (CCl_4) τ 4.10 (d, 2, J = 5 Hz, PhCH=C*H*–), 3.38–2.58 (m, 10, phenyl and PhC*H*=CH–); ir (CCl_4) 2000–1660 (ortho-disubstituted phenyl pattern), 1642, 1422 cm^{-1} (cis olefin); mass spectrum (75 eV) m/e (rel intensity) 216 (100), 217 (19.0), 218 (2.2), 215 (79), 213 (28), 189 (15), 187 (14).

Anal. Calcd for $C_{17}H_{12}$: C, 94.41; H, 5.59. Found: C, 94.12; H, 5.78.

Uv, see Table II; $[\alpha]^{24}\mathrm{D}$ −680.1° (c 0.2566, $CHCl_3$); $[\alpha]^{25}\mathrm{D}$ −638.9° (c 0.3780, CH_3OH); ORD (c 2.247 × 10^{-3}, CH_3OH) [M] (nm) −5430 (400), −60,090 (302), −29,410 (298), −40,700 (295), −30,200 (291), −36,000 (287), 0 (280), +3770 (279), +4540 (276), +39,800 (268), +37,700 (265), +44,900 (260), 0 (249), −69,200 (240), 0 (236), +214,500 (224), +69,400 (212), +166,100 (204); CD (c 2.247 × 10^{-3}, CH_3OH) $[\theta]$ (nm) 0 (400), −50,600 (300), −35,100 (297), −51,000 (292), −48,700 (290), −85,900 (282), −74,200 (277), −81,300 (273), −62,600 (268), −49,100 (262), 0 (252), +33,100 (249), 0 (245), −220,000 (236). 0 (225), +53,300 (221), 0 (211), −29,000 (208), 0 (205).

(*S*)-(−)-1,1′-Spirobiindan (5b). To zinc amalgam prepared as above from 12 g of 20 mesh zinc were added 17 ml of hydrochloric acid, 7 ml of water, and a solution of 0.20 g of (*S*)-(+)-**4** in 12 ml of toluene. This mixture was heated at reflux for 4 days with 5 ml of hydrochloric acid being added every 10 hr. At the end of this time the reaction mixture was poured onto ice and extracted with dichloromethane; the extract was dried ($CaSO_4$) and concentrated under reduced pressure, and the residue was subjected to gas chromatography (10% FFAP on Fluoropack 80 at 160°) to yield 0.13

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[37] "Sadtler Standard Infrared Spectra," Sadtler Research Laboratories Inc., Philadelphia, Pa., 1968, Spectrum 5873.

[38] "Sadtler Standard Nmr Spectra," Sadtler Research Laboratories Inc., Philadelphia, Pa., 1968, Spectrum 3187.

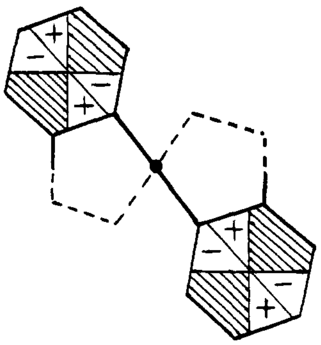

Figure 4. Coupling of transition moments or polarizability axes in the (*R*)-1,1′-spirobiindan nucleus.

g (73%) of the spiran: nmr (CCl_4) τ 7.97–7.68 (m, 4, $PhCH_2CH_2$–), 6.98 (t, 4, J = 8 Hz, $PhCH_2CH_2$–), 3.22–2.75 (m, 8, phenyl); ir (neat) 749 cm^{-1} (ortho-disubstituted phenyl); mass spectrum (70 eV) *m/e* (rel intensity) 220 (100), 221 (18.5), 222 (1.97), 206 (19.7), 205 (30.7), 204 (31.1), 203 (25.2), 202 (18.1).

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.76; H, 7.48.

Uv, see Table II; $[\alpha]^{24}D$ −71.1° (*c* 0.6164, $CHCl_3$), $[\alpha]^{25}D$ −70.5° (*c* 0.8241, CH_3OH); ORD (*c* 2.135 × 10^{-3}, CH_3OH) [M] (nm) −584 (400), −11,250 (277), 0 (274.5), +2200 (275), 0 (272), −4390 (270), 0 (268), +3950 (266), 0 (262), +1760 (259), +7040 (230), 0 (228), −72,400 (223), −56,300 (219), −68,100 (218), −25,600 (208), −54,900 (206), 0 (204); CD (*c* 2.135 × 10^{-3}, CH_3OH) [θ] (nm) 0 (400), −11,950 (274), −3070 (270.5), −7460 (268), −2930 (263), −3810 (260), 0 (245), +42,300 (225), 0 (222), −10,200 (220), −31,000 (216), −48,100 (210), 0 (206).

A sample of the *R*-(+) isomer, prepared from (*R*)-(−)-**8**, $[\alpha]^{27}D$ −24.9° ($CHCl_3$), had identical ir, uv, and nmr spectra and gave almost exactly enantiomeric ORD and CD curves (see Table I); the latter results indicate the absence of instrumental artifacts in the present ORD and CD curves.

Discussion of Results

Optical rotation results when the interaction of light with matter produces electric and magnetic moment changes that are not at right angles to one another.[39–41] Dextrorotation results when these effects are parallel, levorotation when they are antiparallel. In general, such behavior is caused by chiral features of molecular architecture that impose helicity on the motions of electrons; right-handed helical motion gives dextrorotation[42] at long wavelengths and positive Cotton effects at absorption bands.[39] There are several detailed mechanisms for optical activity, and it is now generally accepted that they are not mutually exclusive, but complementary, and capable of melding one into the other over a range of cases. Thus, the one-electron mechanism[43–45] is represented at one extreme by the symmetrical chromophore with its transitions perturbed by the electrostatic effects of a chiral environment and at another by the twisted, inherently chiral chromophore[3] (*e.g.*, hexahelicene[46]). In the helical conductor model,[9,47] the twisted chromophore represents that extreme in which transmission is achieved through a continuous π system, but it is not, in principle, different from the case in which transmission is achieved by a cooperative set of small electronic displacements along a twisted chain of σ bonds. In turn, the latter case represents one of the ways in which a set of oscillators may be coupled, augmenting—or in some case, opposing—the through-space dipole–dipole interactions postulated in the usual coupled oscillator mechanism.[48,49]

Figure 4 shows an analysis of the ways in which local transition moments or polarizability axes can couple in the (*R*)-1,1′-spirobiindan nucleus, assuming that they pass through the centers of the rings. Orientation parallel to the dihedral line formed by intersection of the two indan planes, or to a line passing through the spiro atom, places the two moments or axes in the same plane; such coupling is achiral. Orientation toward the spiro atom is, however, required for effective head-to-tail B-coupling and the signs of the rotatory effects resulting from such coupling are shown in the unshaded areas. The A mode of coupling *may* be preferred in the shaded areas; if so, it will be levorotatory in effect. It is clear, on this basis, that Lowe's prediction that *R* allenes and spirans with C_2 symmetry will be dextrorotatory at long wavelengths[50] cannot be general, even when effects due to extraneous substituents[1b,51] or to simple symmetrical chromophores perturbed by their environment are excluded or taken into account.

Long-Wavelength Rotations. The principal axes of polarizability of indan (**18**) and indene (**19**) would be expected to be essentially along the long axes of the molecules, while that of indanone (**20**) would be directed toward the carbonyl oxygen atom. If so, then, from Figure 4, it would be expected that (*R*)-1,1′-spirobiindane (**5a**) would be dextrorotatory (observed, $[M]_D$ +156°) as would the corresponding spirobiindene (*R*)-**6** (observed for (*S*)-**6** $[M]_D$ −1470°). The monoolefin (*R*)-**9** ($[M]_D$ +470°) has an intermediate rotation, closer to that of the spirobiindan (*R*)-**5a**. This suggests that there may be a more effective B-coupling of the indene residues in the bis(spirobiindene), perhaps a homoconjugative link through atoms 2 and 2′ (see below). The spirobiindanone (*R*)-**4**, on the other hand, might show preferred A-coupling of the principal axes of polarizability (see Figure 4). Alternatively, it might be the other in-plane axis of polarizability of indanone (**21**), perpendicular to the first, that would be involved, now in B-coupling. In *either* case, (*R*)-**4** should be levorotatory (observed for (*S*)-**4**, $[M]_D$ +693°). The monoketone (*R*)-**8** should have an intermediate rotation, which it does [($[M]_D$ −59°).

The distinct levorotation of (*R*)-3,3,3′,3′-tetramethyl-1,1′-spirobiindan (**16**), [M]D −84°, cannot be attributed to any Cotton effects in the accessible ultraviolet since the negative one[19] is so weak that it was missed the first time around[17] and the others are much more strongly positive (see Table I). The methyl groups are symmetrically disposed in pairs with respect to the benzene rings and the spiro atom so that short-range pairwise interactions seem ruled out. When,

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(39) P. Drude, "Theory of Optics" (translated by C. R. Mann and R. A. Milliken), Dover Publications reprint, New York, N. Y., 1959, pp 400–407.

(40) L. Rosenfeld, *Z. Physik*, **52**, 161 (1928).

(41) E. U. Condon, *Rev. Mod. Phys.*, **9**, 432 (1937).

(42) J. W. Gibbs, *Amer. J. Sci.*, 23, 460 (1882).

(43) E. U. Condon, W. Altar, and H. Eyring, *J. Chem. Phys.*, **5**, 753 (1937).

(44) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940).

(45) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, **83**, 4013 (1961).

(46) A. Moscowitz, *Advan. Chem. Phys.*, **4**, 67 (1962).

(47) W. Kauzmann, "Quantum Chemistry," Academic Press, New York, N. Y., 1957, pp 616–636, 703–705.

(48) W. Kuhn, *Z. Phys. Chem.*, *Abt. B*, 20, 325 (1933).

(49) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937); W. W. Wood, W. Fickett, and J. G. Kirkwood, *ibid.*, 20, 561 (1952).

(50) G. Lowe, *Chem. Commun.*, 411 (1965); note that what we have termed *R* spirans would have been designated *S* by Lowe under the old *RS* notation.

(51) G. Krow and R. K. Hill, *ibid.*, 430 (1968).

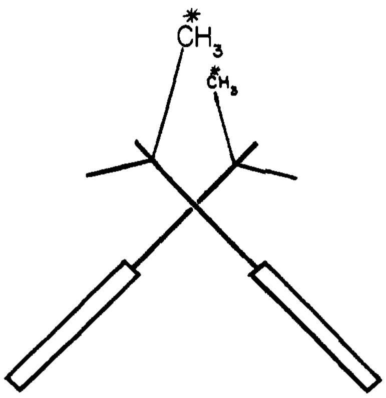
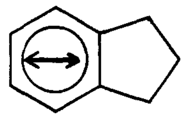


Figure 5. View of (*R*)-3,3,3′,3′-tetramethyl-1,1′-spirobiindan (**16**) along the dihedral axis.



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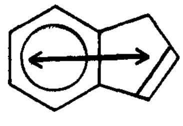

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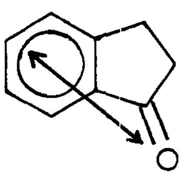

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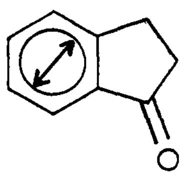

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however, **16** is viewed along the dihedral line formed by intersection of the planes of the indan moieties, it is seen that the two starred methyl groups are termini of a large long-range left-handed helix (Figure 5) (see ref 1b for a similar case). We suggest that this helix pattern, which would not give a Cotton effect in the accessible region of the spectrum, is capable of overriding the aromatic contributions to long-wavelength rotation and making **16** levorotatory.

As seen in Table I, the presence of substituents at positions 5 and 5′ and at 6 and 6′ produces a dextrorotatory effect, presumably by increasing long-axis polarizability and thus enhancing the effect of B-coupling. The strong negative shift produced by bromine atoms at positions 7 and 7′ is noteworthy; it might result from an energetic preference for dipole–dipole A-coupling as seen in Figure 6. We conclude that the long-wavelength rotations of these systems can adequately be accounted for in terms of generally preferred B-, but occasional A-, coupling of the axes of polarizability of the two moieties comprising the spiran structure.

Ultraviolet Cotton Effects. The wavelengths and extinction coefficients for the main ultraviolet absorption bands of the compounds of interest in this work are collected in Table II. Indan and 1-carboxymethyl-1-phenylindan (**7**) (Figure 7) show the benzenoid ^1L_b band[52] near 260 nm, with its vibrational fine structure, considerably intensified as compared, *e.g.*, with tetralin (ϵ max 620) or *o*-diethylbenzene (ϵ max 200),[53] and the ^1L_a band[52] near 215 nm which, in the case of indan, appears to have two components. The same bands are given by 1,1′-spirobiindan (**5**) (Figure 8) with roughly doubled intensity. There is a shoulder on the ^1L_a band at 222 nm, possibly indicating homoconjugation of the two benzene rings; spirobifluorene gives evidence, in the esr spectrum of its anion, of overlap of orbitals of the type required for such interactions.[54] The benzoyl chromophore shows a weak n–π* (ϵ 5–100) band near 320 nm, a stronger (ϵ 1000–2000) ^1L_b band near 290 nm, and a strong (ϵ 10,000) band near 240 nm.[55] These same bands are also present in the spectrum of 1-indanone, but intensified (ϵ 250, 2500, 18,000).[56] The ultraviolet spectra of 3-carboxymethyl-3-phenyl-1-indanone (**3**) (Figure 9) and of 3-oxo-1,1′-spirobiindan (**8**) (Figure 10) are similar to that of indanone;[56] the strong end absorp-

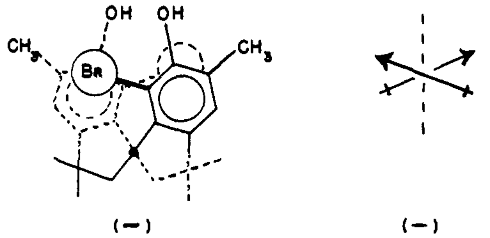

Figure 6. (*R*)-7,7′-Dibromo-6,6′-dihydroxy-3,3,3′,3′,5,5′-hexamethyl-1,1′-spirobiindan.

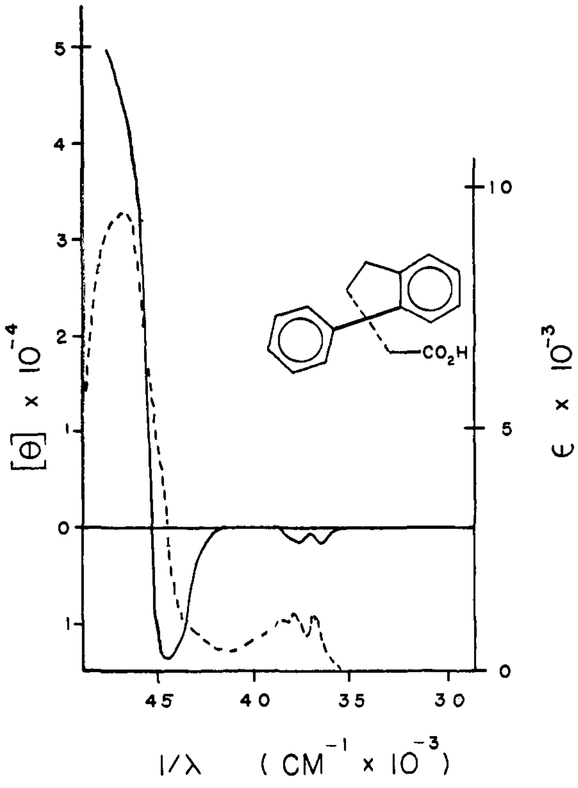

Figure 7. CD (—) and uv (- - -) spectra of (*S*)-(+)-1-carboxymethyl-1-phenylindan (**7**) in methanol.

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(52) Notation of J. R. Platt, *J. Chem. Phys.*, 17, 484 (1949); see H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967, pp 537–548.

(53) W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnold, *Tetrahedron*, 5, 179 (1959).

(54) G. Urry in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, pp 281–288.

(55) H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, pp 256–259, 415–421.

(56) P. Ramart-Lucas and J. Hoch, *Bull. Chim. Soc. Fr.*, 19, 220 (1952).

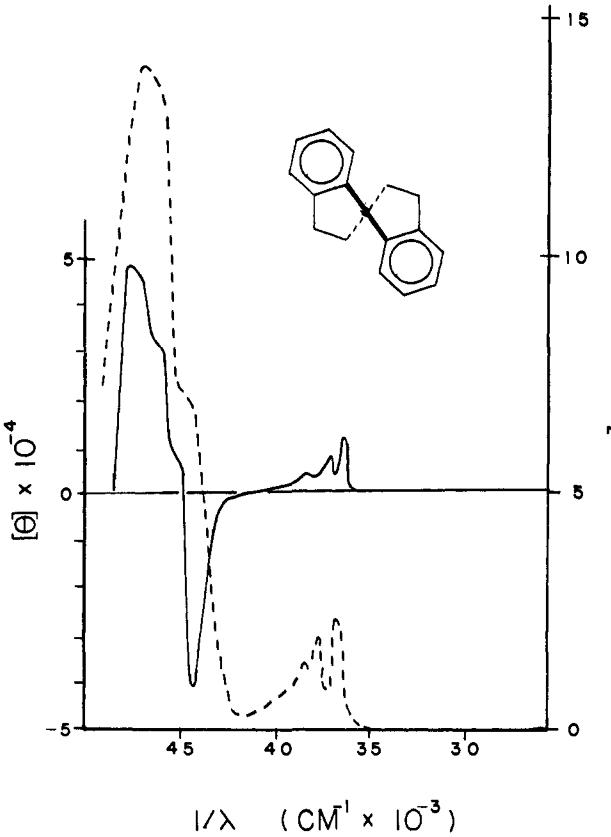

Figure 8. CD (—) and uv (- - -) spectra of (*R*)-(+)-1,1′-spirobiindan (**5a**) in methanol.

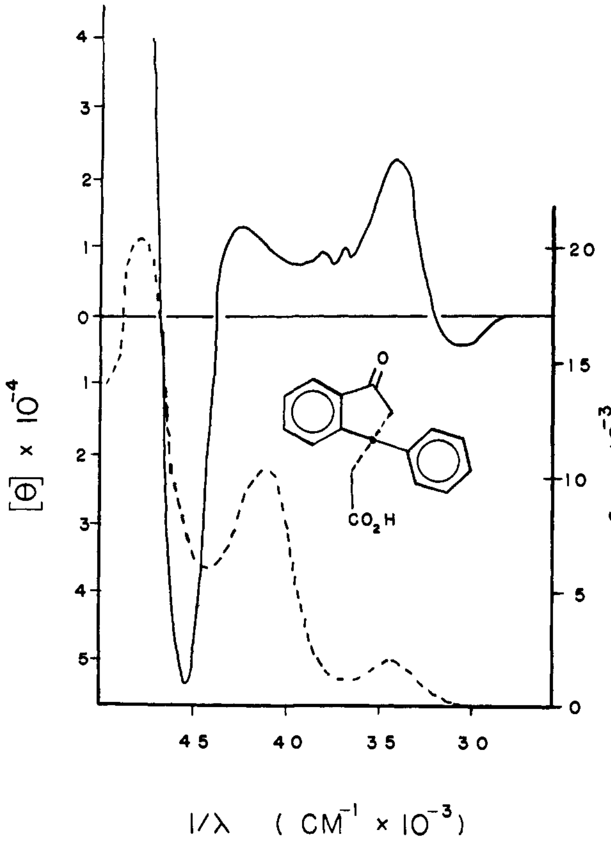

Figure 9. CD (—) and uv (- - -) spectra of (*R*)-(+)-3-carboxymethyl-3-phenyl-1-indanone (**3b**) in methanol.

tion of the latter is seen as a peak at about 210 nm in Figures 9 and 10. We suggest that this latter band,

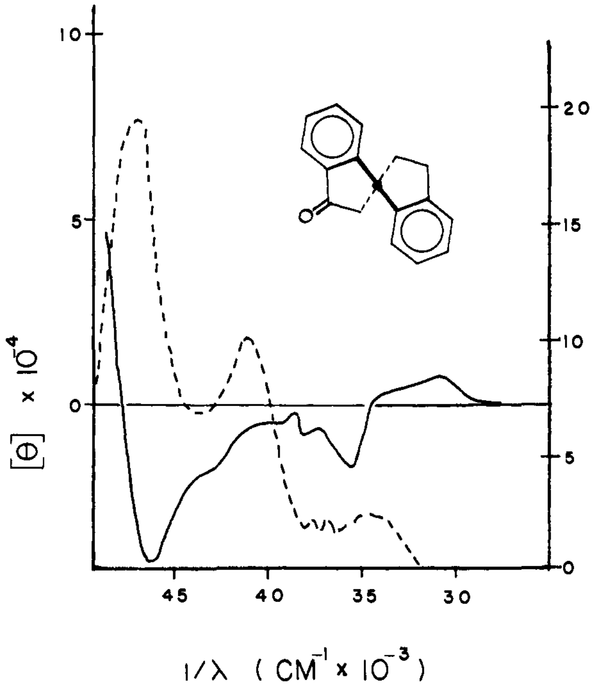

Figure 10. CD (—) and uv (- - -) spectra of (*R*)-(−)-3-oxo-1,1′-spirobiindan (**8**) in methanol.

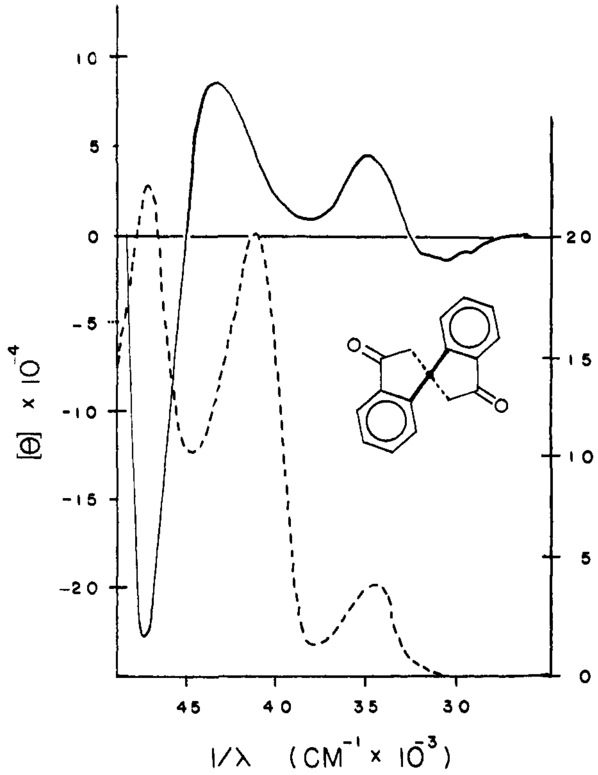

Figure 11. CD (—) and uv (- - -) spectra of (*S*)-(+)-1,1′-spirobi-3-indanone (**4**) in methanol.

which is not much further intensified in the diketone **4** (Figure 11), is due to an aromatic transition related to that producing the ^1L_a band seen in the indans and not strongly influenced by the keto group. The more characteristic benzoyl bands are roughly doubled in intensity in **4** but are not shifted. Indene, the monoindene **9** (Figure 12), and the spirobiindene **6** (Figure 13) likewise show similar spectra. In each case there

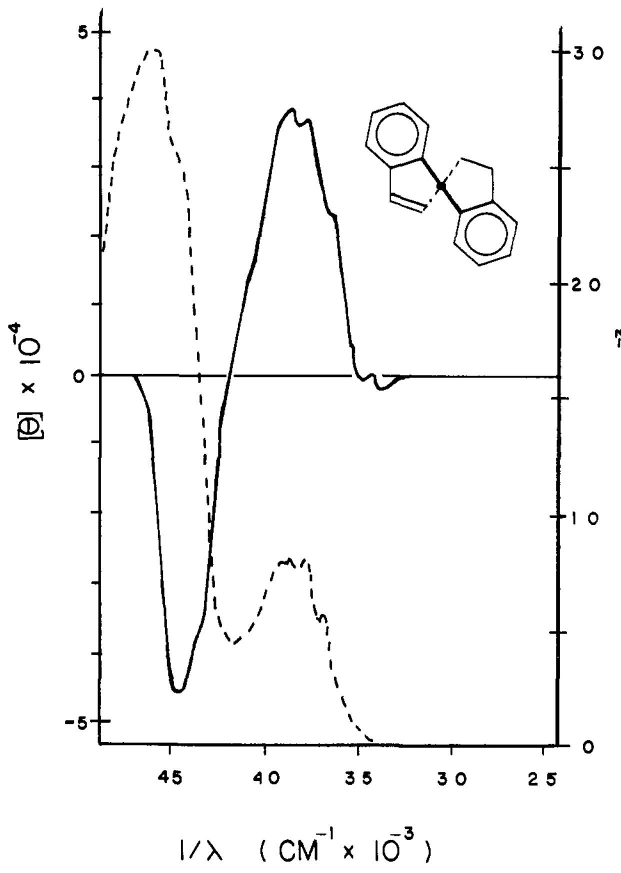

Figure 12. CD (—) and uv (- - -) spectra of (*R*)-(+)-2,3-dihydro-1,1′-spirobiindene (**9**) in methanol.

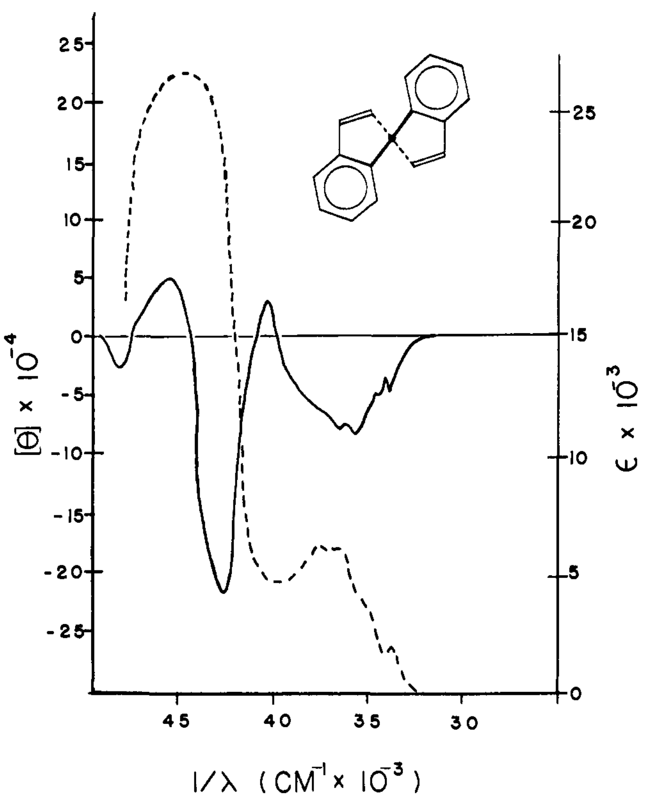

Figure 13. CD (—) and uv (- - -) spectra of (*S*)-(−)-1,1′-spirobiindene (**6**) in methanol.

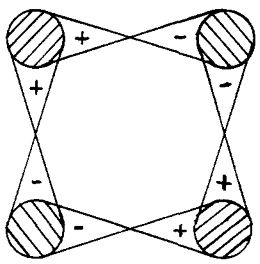

Figure 14. Homoconjugative overlap for certain orbital states of (*S*)-1,1′-spirobiindene (**6**).

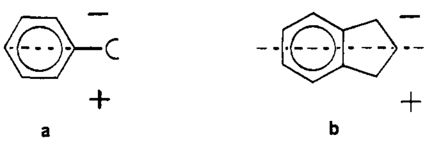

Figure 15. Sector rules for aromatic ^1L_b bands, keyed to the C_2 axis of the ring. Only the signs of upper sectors near the substituents are shown.

is a broad, strong band, giving evidence of fine structure in the region 230–300 nm. In **9** (Figure 12), the shorter wavelength band of the indene moiety overlaps the ^1L_a band of the indan moiety. Only the indene band is seen in 1,1′-spirobiindene (**6**) (Figure 13), shifted somewhat to longer wavelength, suggesting some homoconjugation[54] here as well. Indeed, in this case orbital states in which the orbital symmetry at atoms 2 and 2′ are different from those at 1a and 1a′ (the aromatic carbon atoms attached to the spiro atom) will allow a full homoconjugative overlap (Figure 14).

The ^1L_b bands give rise to relatively large Cotton effects in simple chiral indans;[10,11] these compounds, like monosubstituted benzenes, follow a sector rule keyed to the local C_2 axis of the aromatic ring[10,57] (Figure 15). (The question of whether these rules are quadrant or octant rules is moot so long as they are keyed to the C_2 axis. If they are keyed to transition moments perpendicular to that axis,[57b] then they must become octant rules.) In accord with this rule (Figure 15), we find that (*S*)-(+)-1-carboxymethyl-1-phenylindan (**7**) (Figure 7) gives a negative ^1L_b Cotton effect, the phenyl group presumably outweighing the aliphatic chain. But it is seen in Table I that the ^1L_b Cotton effects of many, *but not all*, of the 1,1′-spirobiindans are positive in the *R* configuration. These compounds, thus, follow, for the most part, the reverse of the rule shown in Figure 15; this reverse rule has been proposed for phthalimides,[58] many alkaloids,[59,60] and for some tetralins and indans.[61] We do not believe that the sector rule of Snatzke and Ho[62] provides a useful solution to this dilemma. Instead, the fact that some of Hagishita's compounds (Table I) show both positive and negative CD peaks in this region, as do $\Delta^{1,3,5(10)}$-estratrien-17β-ol (**22**)[63] and some de-

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(57) (a) G. G. De Angelis and W. C. Wildman, *Tetrahedron*, **25**, 5099 (1969); (b) H. E. Smith and T. C. Willis, *J. Amer. Chem. Soc.*, **93**, 2282 (1971).

(58) J. H. Brewster and S. F. Osman, *ibid.*, **82**, 5754 (1960).

(59) K. Kuriyama, T. Iwata, M. Moriyama, K. Kotera, Y. Hameda, R. Mitsui, and K. Takeda, *J. Chem. Soc. B*, 46 (1967).

(60) G. Snatzke, G. Wollenberg, J. Hrbek, Jr., F. Santavý, K. Bláha, W. Klyne, and R. J. Swann, *Tetrahedron*, **25**, 5059 (1969).

(61) E. Dornhege and G. Snatzke, *ibid.*, **26**, 3059 (1970).

(62) G. Snatzke and P. C. Ho, *ibid.*, **27**, 3645 (1971).

(63) M. Legrand, cited in ref 62.

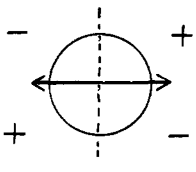
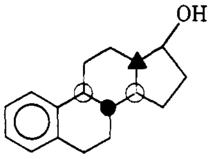


Figure 16. General octant rule for aromatic transitions. Signs for the upper octants shown.

rivatives of phenylalanine,[64] suggests that in some cases *both* rules operate,[57,64] keyed to transition moments at right angles to one another and displaced by differences in vibrational patterns so they do not simply cancel. We concur with Smith and Willis that the systems shown in Figure 15 are keyed to transition moments perpendicular to the C_2 axis, whence the other rules must be keyed along that axis. This leads to a general octant rule for the aromatic nucleus, keyed *only* to the direction of the transition moment (Figure 16). Since this rule is keyed to the bare benzene nucleus, symmetry requires that it be an octant rule.[65] Note that it has the same form as the ketone octant rule.[45] Our results here, then, do not require the postulation of any electronic coupling of the spiroindan ^1L_b transitions, even though the Cotton effects are inverted from those found in monindans, merely a change in the *predominant* mode of vibration of the benzene rings.



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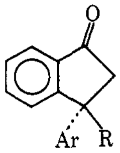
The ^1L_a bands of the spirobiindans with no substituents on the aromatic rings or with substituents only para to the spiro atom show the same basic pattern (Table I) (Figure 8) as simpler monoindans **22**[10,11] and (*S*)-**7** (Figure 7), but with distinctly more intense Cotton effects. Although it is tempting[17–19] to invoke splitting of the absorption band by the coupled oscillator mechanism for the spirobiindans, the essentially parallel results in the indan series[11] indicate that some other mechanism is required to account for splitting of the ^1L_a band. Perhaps this band, too, has *several* transition moments giving rise to components of similar energy that cannot easily be separated spectroscopically but which, by producing oppositely signed Cotton effects, can be discerned by CD spectroscopy. A set of sector rules, keyed either as in Figure 16 or in the reverse fashion, might well accommodate this situation, but more data are needed to clarify it. The ^1L_a sector rules of DeAngelis and Wildman[57a] (the obverse of their ^1L_b rule) and of Verbit and Price[66] appear to be contradictory, suggesting that they are keyed to transition moments with different orientations relative to the bond between the phenyl group and the asymmetric center. If so, it seems likely, from the latter data,[66] that the ^1L_a octant rule will have a pattern opposite that shown in Figure 16, assuming normal ^1L_a orientation of the transition moment along the line of that bond.

The CD spectra of configurationally related 1-indanones are presented in Table III and in Figures 9, 10, and 11. It is evident that the long-wavelength CD maxima, associated with the benzoyl chromophore bands near 327 nm (n → π*) and 290 nm (^1L_b), are about twice as strong in the diketone **4** (Figure 11) as in the monoketones and of the same sign. This indicates that the transitions involved do not couple in this system. The CD maximum for the benzoyl ^1L_a band is, however, in every case at a considerably lower wavelength than the absorption maximum; it is most strongly shifted, and is greatly enhanced, in the diketone. This suggests that some components of that band are coupling or mixing, in a chiroptically significant way with lower lying bands. Given the probable orientation of the ^1L_a transition moment in indanone (**20**) an A-coupling (levorotatory) might be preferred energetically. The corresponding B-coupling of this moment would be less favored and so give a positive Cotton effect at a lower wavelength. The short-wavelength positive Cotton effects in the monoketone **8** (Figure 10) and diketone **4** (Figure 11) may originate in this way. The negative Cotton effects at 210–212 nm in **3** (Figure 9) and **8** are probably related to the aromatic ^1L_a band. The origin of the positive Cotton effect at 220 nm is uncertain; the effect is probably not due to the carboxy group, for conversion to the salt has little effect. Of the characteristic bands of 1-indanone, then, we conclude that the strong bands contain components, probably resulting from mixing with other bands, that can couple, leading to CD bands considerably shifted from the principal peaks of those bands.

Table III. CD Spectra of Configurationally Related 1-Indanones



λ, nm ([θ] × 10^{-3}) (methanol)			
(*S*)-(−)-**3a**[a]	(*S*)-(−)-**3a**[a] K⁺ salt	(*R*)-(−)-**8**	(*R*)-(−)-**4**[a]
327 (+5.9)	325 (+6.8)	327 (+8.0)	328 (+12.3)
295 (−23.1)	296 (−24.4)	281 (−19.5)	286 (−49.8)
235 (−12.4)	235 (−14.4)	235–228[b] (−16.3 to −21.1)	230 (−90.0)
220 (+54.4)	220 (+47.7)		
212 (−40.9)[c]	210 (−60)[c]	216 (−43.4)	
		204 (+32.1)[c]	212 (+230)

[a] Enantiomer actually used. [b] Shoulder. [c] Final reading.

(*R*)-(+)-2,3-Dihydro-1,1′-spirobiindene (**9**) shows a positive Cotton effect (Figure 12) with two peaks at 264 and 260 nm ([θ] +36,400, +38,900, respectively). The absorption peak at 218 nm, with a shoulder at 222 nm, gives a negative Cotton effect at 224 nm ([θ] −45,700), suggesting that there may be two independently acting components to this peak. (*S*)-(−)-1,1′-Spirobiindene (**6**) (Figure 13) has a more or less enantiomeric CD spectrum, as is to be expected. The long-wavelength

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(64) J. Horwitz, E. H. Strickland, and C. Billups, *J. Amer. Chem. Soc.*, **91**, 184 (1969).

(65) J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966).

(66) L. Verbit and H. C. Price, *J. Amer. Chem. Soc.*, **94**, 5143 (1972). We thank Dr. Verbit for sending us a copy of this manuscript before publication.

band seems to be split, with maxima at 282 nm ([θ] −85,900) and 249 nm ([θ] +33,100). The lower wavelength band, which the uv spectrum suggests might arise from homoconjugation, is also strongly split with CD peaks at 236 nm ([θ] −220,000) and 221 nm ([θ] +53,300). This indicates that these two indene transitions are capable of a preferred long-axis B-mode coupling (levo in the *S* enantiomer) and an energetically less favored A-mode. The high rotatory power shown in these CD peaks indicates that homoconjugation as shown in Figure 14 may augment this coupling. If so, this system exhibits simultaneously the characteristics of a coupled oscillator and a twisted composite chromophore.

We conclude that studies of the chiroptical properties of suitable sets of "monomeric" and "dimeric" chromophoric systems can, indeed, provide detailed insights into the ways in which these chromophores respond to light[2]–insights available at present in no other way.

Dissymmetric Spirans. II.[1] Absolute Configuration of 1,1′-Spirobiindene and Related Compounds[2]

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Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30601. *Received June 20, 1972*

Abstract: The optically active spirans, 1,1′-spirobiindan, 1,1′-spirobiindene, and 1,1′-spirobiindan-3-one, have been prepared from optically active 3-carboxymethyl-3-phenyl-1-indanone, an intermediate possessing centrodissymmetry. Correlation of its configuration with two independent standards of absolute configuration, 2-methyl-2-phenylsuccinic acid and 1-cyclohexyl-1-phenylethanol, allowed unambiguous assignment of absolute configuration to the series of spiroindans. The spectroscopic properties of the spiro compounds, which show evidence of spiroconjugation, are discussed.

The determination of absolute configuration of molecules possessing axial symmetry, *i.e.*, those which are dissymmetric but not asymmetric,[4] continues to pose intriguing problems because of the absence of a formal asymmetric carbon which might serve as the basis for configurational correlations. Molecules of C_2 symmetry, such as allenes, spirans, hindered biphenyls, hexahelicene, and *trans*-cyclooctene, are of particular interest, and ingenious solutions have been provided for these cases by both chemical[5] and crystallographic[6] methods.

Because of their relatively rigid geometry, spirans offer the opportunity to study interactions between functional groups held in fixed relative orientations, and consequently are useful substrates for chiroptical studies. Unambiguous assignments of absolute configuration to chiral C_2 spirans were not made until 1968–1969, when configurations were established for spirans **1**[1], **2**,[7] and **3**.[8] More recently, assignments of absolute configuration have been made to spirans **4**,[9] **5**,[10] and **6**,[11] using empirical rules or deductions from chiroptical properties. In compounds **1**, **3**, and **4** the spiro atom is bonded to four methylene groups; not surprisingly there is no evidence of electronic interaction between the two rings and the optical rotations are generally modest. Only in **2** and **5** was it possible to relate rotatory dispersion to absolute configuration.[7b,10] Consequently it appeared worthwhile to investigate spiran systems in which aromatic rings and other unsaturated chromophores were linked directly to the spiro carbon, leading to enhancement of rotatory strengths and possibly detection of spiroconjugation[12,13] in ORD as well as uv spectra. We undertook the preparation, resolution, and determination of absolute configuration of 1,1′-spirobiindene (**7**). While this work was in progress Professor J. H. Brewster informed us of similar studies on **7** and its derivatives in his laboratory.[14] Very recently an extensive series of optically active tetramethyl-1,1′-spirobiindans of structure **8** as well as the spirobiindanol **9** has been reported, and absolute configurations were assigned both by theoretical calculations of ORD spectra and by X-ray analysis.[15–17]

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[1] For the first paper in this series, see G. Krow and R. K. Hill, *Chem. Commun.*, 430 (1968).

[2] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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