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Synthesis, Absolute Configuration, and Chiroptical Property of (+)-*cis*-4b,5,9b,10-Tetrahydroindeno[2,1-*a*]indene-5,10-dione

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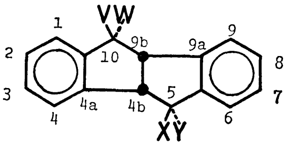
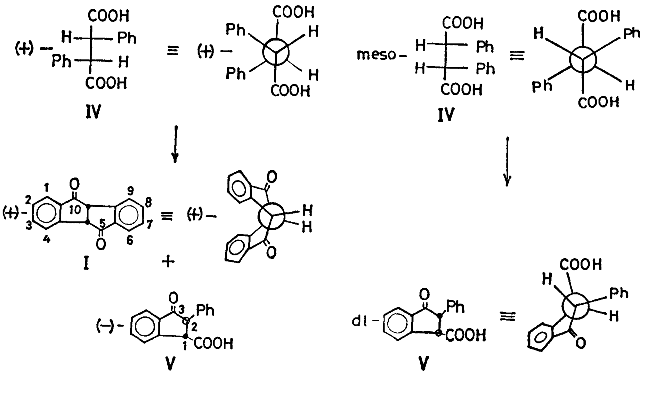
Synopsis. The title compound having the (4b*S*,9b*S*) configuration was prepared from (2*S*,3*S*)-(+)-2,3-diphenylsuccinic acid, and the circular dichroic property was discussed.

The title compound (I) has a fairly rigid *cis*-bicyclo[3.3.0]octane skeleton and holds two 1-indanone chromophores in a twisted spacial position. This paper deals with the synthesis, determination of the absolute configuration, and the chiroptical property of (+)-I.



I, V+W=X+Y=O
II, V=W=H, X+Y=O
III, V=W=X=Y=H

The route of synthesis was outlined in Scheme 1. (2*S*,3*S*)-(+)-2,3-Diphenylsuccinic acid (IV)[1,2] was converted to the dichloride, which was subjected to the Friedel-Crafts reaction to yield (+)-I. Thus, the absolute configuration of (+)-I was determined to be (4b*S*,9b*S*). As a by-product of the cylization, (−)-keto acid (V) was obtained. The keto acid was subjected again to the same cyclization reaction, but virtually recovered unchanged. Under the more drastic condition using hot polyphosphoric acid, (−)-V afforded (+)-I having somewhat low optical purity. The only product isolated from the same Friedel-Crafts reaction of *meso*-IV was *rac*-V. On the basis of these facts, (−)-V was tentatively assigned to be (1*S*,2*S*)-(−)-3-oxo-2-phenyl-1-indancarboxylic acid, in which the configuration between the phenyl and carboxyl groups would be trans, being unable to proceed to further cyclization. The trans isomer seemed to be thermodynamically more stable than the cis one and to be produced from (+)-IV during the course of transformation (not before but after the half cyclization) by epimerization at the C-2 chiral center α to both phenyl and carbonyl groups. The Clemmensen reduction of (+)-I gave monoketone (II) and hydrocarbon (III), both of which had (4b*S*,9b*S*) configuration.



Scheme 1.

The UV and CD spectra of (+)-I are shown in Fig. 1. A negative CD band with fine structure and a positive one were observed in the n-π^* and $^1B_{2u}$ regions, respectively. A typical negative couplet centered at near 40000 cm^{-1} was attributed to an exciton couplet due to the interaction of so-called intramolecular CT band of two benzoyl chromophores. From a consideration using the Dreiding molecular model with the (4b*S*,9b*S*)-configuration, the negative and positive peaks could be assigned to the transitions from the ground to the excited states with A and B symmetry, respectively. The transition moment of the monomeric indanone chromophores was assumed to lie in the center of the benzene ring and to be directed to the oxygen atom. This interpretation was supported by UV intensity distribution *versus* wavelength in the band, and with the lack of a CD couplet in the same absorption region of monoketone II.[3]

Thus, the absolute configuration deduced from the CD analysis was in accord with the chemically established (4b*S*,9b*S*) configuration.

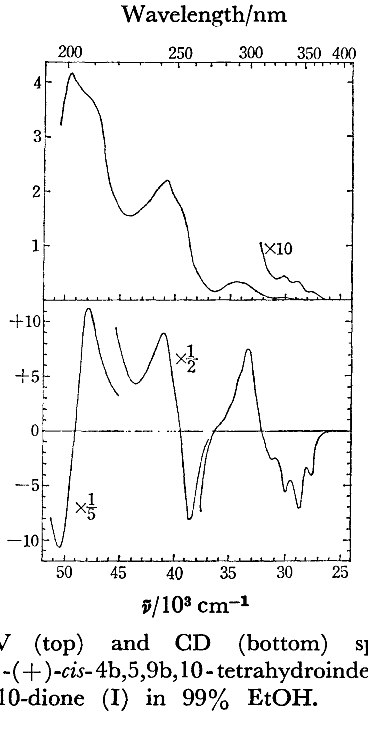


Fig. 1. UV (top) and CD (bottom) spectra of (4b*S*,9b*S*)-(+)-*cis*-4b,5,9b,10-tetrahydroindeno[2,1-*a*]indene-5,10-dione (I) in 99% EtOH.

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Experimental

Melting points were measured on a Mettler FP2 apparatus and were uncorrected. IR spectra (Nujol mull) were obtained on a Hitachi EPI-2, EPI-G$_3$, or a JASCO DS-301 spectrometer, and UV spectra on a Hitachi EPS-3T spectrometer. ^{1}H-NMR spectra of CDCl$_3$ solutions were obtained on a Varian XL-100 or A-60D spectrometer, and chemical shifts from internal TMS are given in δ-unit. Optical rotations were measured on a Union Giken Polarimeter PM-71 at 20 °C, and CD spectra on a JASCO J-20 spectrometer. Shoulders and inflections are denoted by an asterisk.

2,3-Diphenylsuccinic Acid (IV): *dl*-Form,$^{1)}$ recrystallized from water, melted once at 184—185 °C, immediately resolidified and melted again at 233—236 °C, and had IR: 1700 ($\nu_{C=O}$)cm^{-1}, ^{1}H-NMR: 4.38 (s, 2H, methine), 7.27 (s, 10H, aromatic), 7.40 (s, 2H, COOH). *meso*-Form,$^{1)}$ recrystallized from 99% EtOH, melted at 248—252 °C, and had IR: 1690 ($\nu_{C=O}$)cm^{-1}, ^{1}H-NMR (DMSO-d_6): 4.26 (s, 2H, methine), 7.20—7.54 (m, 10H, aromatic), 12.22 (br s, 2H, COOH).

The racemate was resolved *via* bis-brucine salt.$^{1)}$ An optically pure salt melted at 154.5—155.5 °C. Found: C, 64.59; H, 6.92; N, 4.69%. Calcd for $C_{62}H_{66}N_4O_{12}\cdot 5H_2O$: C, 64.79; H, 6.67; N, 4.87%. (*S*)-(+)-Form,$^{1,2)}$ recrystallized from water, melted once at 170—180 °C, resolidified immediately and melted again at 210—220 °C. The hygroscopic acid was analysed immediately after drying at 100 °C for 17 h *in vacuo*, and had $[\alpha]_D$ +361.0° (*c* 1.457, 99% EtOH). Found: C, 70.82; H, 5.29%. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22%.

*(4b*S*,9b*S*)-(+)-*cis*-4b,5,9b,10-Tetrahydroindeno[2,1-*a*]indene-5,10-dione (I) and (−)-3-Oxo-2-phenyl-1-indancarboxylic Acid (V)*: A mixture of (*S*)-(+)-IV (0.655 g, 2.34 mmol) and PCl$_5$ (1.2 g, 5.8 mmol) was warmed on a boiling water bath for 30 min. After removal of POCl$_3$ *in vacuo*, the residue was dissolved in CS$_2$ (65 ml) and cooled in an ice bath. Freshly powdered AlCl$_3$ (1 g) was added at once, and the mixture was heated under reflux for 30 min with stirring. The reaction was quenched carefully by addition of ice water and 3M-HCl, and the product was extracted with ether. The combined organic layers were washed three times with aq 5% NaHCO$_3$ and dried over Na$_2$SO$_4$. The solvents were removed under reduced pressure to afford crude crystals (0.277 g) of (+)-I, which were recrystallized from EtOH. (*S*)-(+)-Diketone (I) sublimed at *ca.* 240 °C, melted at 253.5—254.5 °C, and had $[\alpha]_D$ +51.1°, $[\alpha]_{405}$ −600° (*c* 0.0572, 99% EtOH); IR: 1710 ($\nu_{C=O}$) cm^{-1}; UV: $\lambda_{max}^{99\%\ EtOH}$ (ε) 364 (164), 346 (346), 332.5 (392), 297* (3220), 291 (3310), 253* (17000), 245.5 (21300), 237* (23500), 210* (36800), 202 (42500) nm; CD: $\lambda_{max}^{99\%\ EtOH}$ ($\Delta\varepsilon$) 362 (−4.00), 348 (−7.12), 333 (−5.42), 320 (−2.60), 299 (+7.29), 258.5 (−16.8), 243.5 (+18.9), 209 (+56.8), 198 (−54.8) nm. Found: C, 81.96; H, 4.27%. Calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%. The combined NaHCO$_3$ washings were acidified with concd HCl, and light yellow solid (0.273 g) thus obtained was recrystallized from CCl$_4$ to yield (−)-V; mp 138—139 °C; $[\alpha]_D$ −150.3°; $[\alpha]_{405}$ −496.9° (*c* 0.192, 99% EtOH); IR: 1725 ($\nu_{C=O}$, ketone), 1690 ($\nu_{C=O}$) cm^{-1}; ^{1}H-NMR (DMSO-d_6): 4.26 (d, *J*=4.5 Hz, 1H, methine), 4.42 (d, *J*=4.5 Hz, 1H, methine), 7.10—7.94 (m, 9H, aromatic); UV: $\lambda_{max}^{99\%\ EtOH}$ (ε) 335* (110), 293 (1820), 287* (1800), 244 (9500), 208 (24200) nm; CD: $\lambda_{max}^{99\%\ EtOH}$ ($\Delta\varepsilon$) 345* (−0.76), 331 (−1.06), 318 (−0.96), 292.5 (−0.86), 285 (−0.78), 269 (−0.35), 244 (−6.12), 220 (+7.58), 210 (+6.66) nm. Found: C, 76.07; H, 4.76%. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80%.

(−)-Keto acid (V, 110 mg) was converted to the acid chloride with SOCl$_2$ in benzene and subjected again to the same cyclization. Only a minor amount (11 mg) of (+)-I was isolated, and almost all of (−)-V was recovered.

Polyphosphoric acid (5 g) was mixed with (−)-V (50.3 mg) and heated on a boiling water bath for 15 h. After ordinary work up, (+)-I (40.3 mg, optical purity *ca.* 40%) was obtained as a neutral product.

rac-3-Oxo-2-phenyl-1-indancarboxylic Acid (V): By the essentially same cyclization reaction of *meso*-IV as in the case of (*S*)-(+)-IV, *dl*-V was obtained, mp 124—126 °C. Neither *dl*-I nor its *trans*-isomer was isolated.

*(4b*S*,9b*S*)-*cis*-4b,5,9b,10-Tetrahydroindeno[2,1-*a*]indene (III) and -5-one (II)*: (*S*)-(+)-Diketone (I, 200 mg) was dissolved in benzene (5 ml) and added to a mixture of water (1 ml), concd HCl (1 ml), and amalgamated Zn, which was prepared by the standard procedure from granules of Zn (1 g). The reaction mixture was refluxed for 6 h with stirring, and the product was extracted with CH$_2$Cl$_2$ after dilution with water. After usual work up, the solvent was removed *in vacuo*, and the residue was chromatographed on a column of silica gel (20 g) using benzene as an eluant. Hydrocarbon III (30 mg), monoketone II (55 mg), and recovered I (90 mg) were eluted successively. Both of II and III were purified by vacuum sublimation and then recrystallization from EtOH. Hydrocarbon III showed mp 140 °C; ^{1}H-NMR: 2.9—4.2 (m, 6H, aliphatic), 7.0—7.7 (m, 8H, aromatic); UV: $\lambda_{max}^{99\%\ EtOH}$ (ε) 273.5 (3880), 267 (2970), 261 (1780), 254 (890), 217.5 (17200), 212.5 (18900), 209 (20200), 196 (64800) nm; CD: $\lambda_{max}^{99\%\ EtOH}$ ($\Delta\varepsilon$) 272.5 (−1.7), 265 (−1.4), 260 (−1.0), 220.5 (+12), 197 (+67.4) nm. Found: C, 93.24; H, 6.81%. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84%.

Monoketone II melted at 120 °C, and had ^{1}H-NMR: 3.0—4.1 (m, 4H, methylene and methine), 7.0—7.4 (m, 8H, aromatic); UV: $\lambda_{max}^{99\%\ EtOH}$ (ε) 332 (295), 294 (2200), 286 (2160), 276 (3100), 269 (2630), 247 (12400), 208.5 (29500) nm; CD: $\lambda_{max}^{99\%\ EtOH}$ ($\Delta\varepsilon$) 362 (+0.15), 346 (+0.39), 331 (+0.50), 316 (+0.46), 305 (+0.37), 291 (+1.2), 285* (+0.98), 275 (−3.4), 268 (−3.9), 251 (−7.2), 230* (+1.4), 206 (+38.1) nm.

References

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2) R. Buchan and M. B. Watson, *J. Chem. Soc., C*, **1968**, 2465; N. D. Berova and B. J. Kurtev, *Tetrahedron*, **25**, 2301 (1969).

3) A positive couplet was anticipated for an exciton interaction of the short axis polarized transition of two 1-indanones. The strongest positive couplet observed at near 49000 cm^{-1} and the positive peak in $^1B_{2u}$ band might be attributed to the coupling of this nature. However, further interpretation of CD is reserved until the exact molecular structural parameters and nature of the electronic transition are clarified.