Absolute Configuration of 1,5-Disubstituted 9,10-Dihydro-9,10-ethenoanthracenes as revealed by Chemical Correlation

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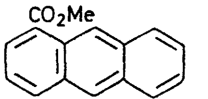
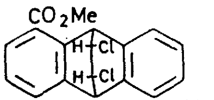
Summary The absolute configuration of (+)-1,5-dicarboxy-9,10-dihydro-9,10-ethenoanthracene (IV) was shown to be 9*R*,10*R* by chemical correlation with (−)-2,5-diacetoxy-7-carboxytriptycene (V) whose configuration was proved to be 1*S*,6*R* by *X*-ray analysis by the Bijvoet method combined with chemical correlation.

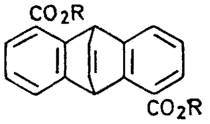
9,10-Dihydro-9,10-etheno- and ethano-anthracene derivatives substituted dissymmetrically in the benzene rings are chiral compounds which have fairly rigid and definite geometry, and may be used as a model compound for the study of optical rotatory properties. *cis*-Dichloroethylene and 1,5-dimethoxycarbonylanthracene (I) were heated in a sealed tube at 180—185° to afford the *cis*-dichloro-adduct (II), m.p. 205°. Treatment of (II) with Zn–Cu couple in boiling methanol gave the etheno-ester (III), m.p. 151°. Addition of *trans*-dichloroethylene to (I) afforded two isomeric *trans*-dichloro-adducts, which were converted by a similar dechlorination reaction into the same etheno-derivative (III). The ethenodicarboxylic acid (IV) obtained by hydrolysis of (III) was resolved with strychnine to yield pure (−)-enantiomer, m.p. 315—322° (decomp.), $[\alpha]_D$



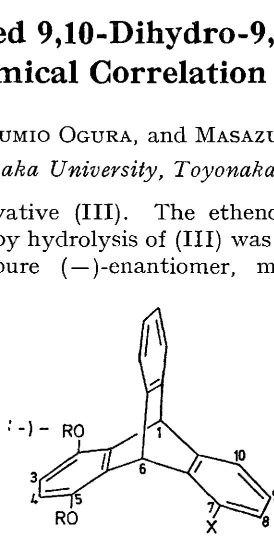
(I)



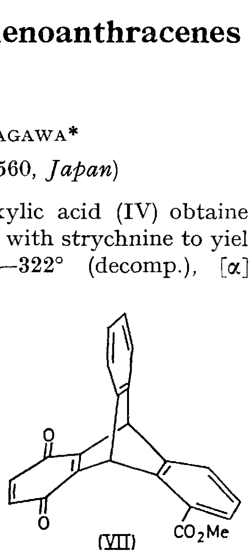
(II)



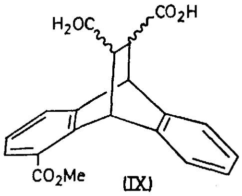
(III; R = Me)
(IV; R = H)



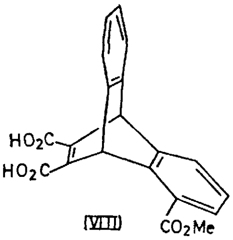
(V; R = Ac, X = CO2H)
(VI; R = H, X = CO2Me)



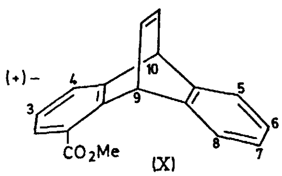
(VII)



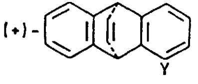
(IX)



(VIII)



(X)



(IV; X = Y = CO2H)
(III, X = Y = CO2Me)
(XI; X = CO2H, Y = CO2Me)
(XII; X = NH2, Y = CO2Me)

$-333{\cdot}3°$ (*c* 0·237, dioxan) and the (+)-enantiomer in somewhat low optical purity.[1]

From optically pure (−)-(IV), a series of 1,5-disubstituted etheno- and ethano-derivatives retaining a C_2 axis of symmetry was prepared.[1] The preceding communication reports c.d. studies on these compounds. The present communication deals with the determination of absolute configuration of (+)-(IV) by chemical means.

The configuration of (−)-2,5-diacetoxy-7-carboxytriptycene (V)[2] has been determined as 1*S*,6*R* by chemical correlation with (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide[3] whose absolute configuration was proved to be 1*R*,6*S* by *X*-ray analysis by the Bijvoet method.[4] Compound (−)-(V) was converted by the usual methods into (−)-(VI) which on potassium bromate oxidation afforded the quinone, (−)-(VII). Mild oxidative cleavage of the quinone ring in (VII) by ammonium persulphate[5] gave the etheno-dicarboxylic acid methyl ester (VIII), which was catalytically reduced to the ethano-derivative (IX). A solution of (IX) in aqueous pyridine was electrolysed in the presence of triethylamine[6] to yield the (+)-etheno-ester (X), m.p. 115·9—116·5° $[\alpha]^{20}_{350}$ + 1181° (*c* 0·007045, EtOH), λ_{max} (99% EtOH) ($\Delta\epsilon$) 303 (+ 2·10), 278·5 (−0·14), 269 (+ 2·26), 262 (+2·38), 227·5 (+ 38·72), 200 nm (−39·58). The (+)-dicarboxylic acid (IV) [optical purity, 87·3%, $[\alpha]^{20}_{D}$ + 291·2° (*c* 0·215, dioxan)] was converted into the (+)-dimethyl ester (III) which was hydrolysed with equimolar aqueous sodium hydroxide to give the (+)-half-ester (XI). From (+)-(XI), Curtius reaction to (XII) and diazotization followed by reduction of the diazonium salt afforded optically pure (+)-(X), m.p. 115·7—116·0°, $[\alpha]^{20}_{350}$ + 1197° (*c* 0·007115, EtOH), λ_{max} (99% EtOH) ($\Delta\epsilon$) 303 (+ 1·84), 278·5 (− 0·15), 269 (+ 2·25), 262 (+ 2·25), 227·5 (+ 37·60), 200 nm (−40·18), indicating that fractionation of the (+)-enantiomer occurs during the course of the transformation.†

The absolute configuration of (+)-(IV) was clearly demonstrated to be 9*R*,10*R* from the identical properties of the (+)-1-methoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene (X) obtained from both processes.

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† All compounds described gave satisfactory elemental analyses and their n.m.r. and i.r. spectra were consistent with the assigned structures.

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