

## Absolute Stereochemistry of 2,2'-Spirobi-indane-1,1'-diols as determined by the C.D. Exciton Chirality Method

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The absolute configurations of *cis,trans*- and *trans,trans*-2,2'-spiropi-indane-1,1'-diols were non-empirically determined by applying the c.d. exciton chirality method to their bis[*p*-dimethylamino]benzoates].

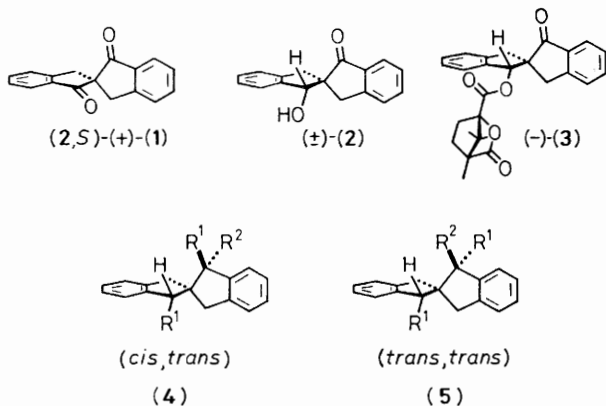
The circular dichroism of chiral spirocyclic compounds with  $\pi$ -electron systems has been intensively investigated<sup>1</sup> as a tool for studying non-bonded homoconjugation between two  $\pi$ -electron chromophores. Dynesen reported the optical resolution of 1'-hydroxy-2,2'-spiropi-indane-1-one (**2**).<sup>2</sup> However, the relative and absolute stereochemistry of (**2**) and related compounds remained unknown. We report a simple and unambiguous chiroptical determination of the absolute configurations of the 2,2'-spiropi-indane-1,1'-diols (**4a**) and (**5a**) by application of the c.d. exciton chirality method, which establishes the stereochemistry of (**2**) and also corroborates the (2*S*) absolute configuration of (+)-2,2'-spiropi-indane-1,1'-dione (**1**).<sup>3</sup>

The racemic alcohol (**2**) was resolved as its  $\omega$ -camphanate ester.<sup>2</sup> Reduction of the  $\omega$ -camphanate ester (**3**),  $[\alpha]_D^{20} -90.12^\circ$  (*c* 0.2996, CHCl<sub>3</sub>) {lit.,<sup>2</sup>  $[\alpha]_D^{20} -89.75^\circ$  (*c* 2.0, CHCl<sub>3</sub>)} with

LiAlH<sub>4</sub> gave a mixture of glycols (**4a**) and (**5a**) (ratio 4:1). The glycols were separated by recrystallization from benzene<sup>2</sup> and by repeated preparative t.l.c. on silica gel (CHCl<sub>3</sub>-MeOH 15:1), followed by derivation to the (*p*-chloro-) and (*p*-dimethylamino-)benzoates. The *cis,trans*-configuration of (**4a**)—(**4c**) was easily assigned from the <sup>1</sup>H n.m.r. spectra (CDCl<sub>3</sub>) which exhibit two peaks for the methine protons, 1-H and 1'-H [(**4a**),  $\delta$  4.56 and 5.22; (**4b**),  $\delta$  6.12 and 6.82; (**4c**)  $\delta$  6.08 and 6.83]. The c.d. spectrum of the *cis,trans*-dibenzoate (**4c**) clearly exhibits exciton split Cotton effects of negative exciton chirality, which lead to a left-handed screw relationship between the two benzoate groups (Figure 1). The (1*R*,1'*S*,2*S*) absolute configuration of (**4a**) was thus determined in a non-empirical manner. Since oxidation of (**4a**) gave (+)-(**1**), the (2*S*) absolute configuration of (+)-(**1**) was established. The present result is in agreement with that obtained from n.m.r. studies of organometallic compounds.<sup>3</sup>

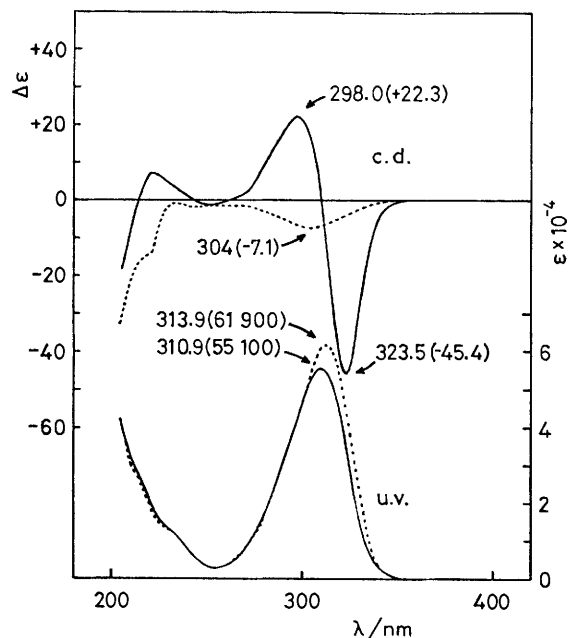
The (1*R*,1'*R*,2*S*) absolute configuration of (**5a**) was determined as follows; since the <sup>1</sup>H n.m.r. spectra of (**5a**)—(**5c**) contain the methine protons, 1-H and 1'-H, as one singlet peak, the structure has C<sub>2</sub>-symmetry. Reduction of (-)-(**3**) with LiAlD<sub>4</sub> gave (**4d**) and (**5d**), which were individually benzoylated. In the <sup>1</sup>H n.m.r. spectrum of (**4d**), the signal at  $\delta$  4.56, which is one of the two methine peaks, disappeared while the other methine signal at  $\delta$  5.22 remained. It is evident that the signal at lower magnetic field is due to the *cis*-methine proton which experiences a paramagnetic 1,3-interaction from a hydroxy-group. A similar phenomenon was observed in the case of (**4e**). These results indicate the presence of a *cis*-methine proton originally, while the *trans*-methine proton was introduced later by the reduction. Therefore, it is established that (**2**) and (-)-(**3**) have a *trans*-configuration and hence that (**5a**) has a *trans,trans*-configuration because of C<sub>2</sub>-symmetry.

The c.d. and u.v. spectra of the dibenzoate (**5c**) also support the *trans,trans*-configuration; the c.d. spectrum shows a weak unsplit Cotton effect, which indicates that the exciton chirality between two benzoate groups is nil (Figure 1). Therefore, the



For (**4**) and (**5**):

	R <sup>1</sup>	R <sup>2</sup>
<b>a</b>	OH	H
<b>b</b>	OCOC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Cl	H
<b>c</b>	OCOC <sub>6</sub> H <sub>4</sub> - <i>p</i> -NMe <sub>2</sub>	H
<b>d</b>	OH	D
<b>e</b>	OCOC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Cl	D



**Figure 1.** The c.d. and u.v. spectra of (1*R*,1'*S*,2*S*)-(4*c*) (solid line) and (1*R*,1'*R*,2*S*)-(5*c*) (dotted line) in ethanol.

angle between two electric transition moments should be  $0^\circ$  (*cis,cis*-configuration) or  $180^\circ$  (*trans,trans*-configuration). As discussed in the preceding communication,<sup>4</sup> it has been shown

that in exciton coupling systems, if the angle between two electric transition moments is larger than  $90^\circ$ , the u.v.  $\lambda_{\max}$  is shifted to longer wavelengths, while if the angle is less than  $90^\circ$ , the u.v.  $\lambda_{\max}$  is shifted to shorter wavelengths. The u.v. spectrum of (5*c*) exhibits a red shift ( $\lambda_{\max}$  313.9 nm) in comparison with that of (4*c*) ( $\lambda_{\max}$  310.9 nm), the angle of which is *ca.*  $90^\circ$ . Therefore, a *trans,trans*-configuration with an angle of  $180^\circ$  is assigned to (5*c*).

Since the absolute configuration of the spiro centre is the same as in (4*a*), *i.e.*, (2*S*), the absolute configurations of (–)-(3) and (5*a*) were determined to be (1*R*, 2*S*) and (1*R*, 1'*R*, 2*S*), respectively.

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