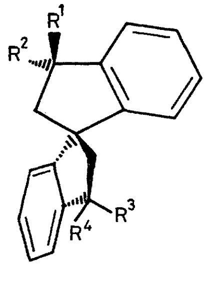
Conformation Dependence of Circular Dichroism of 1,1′-Spirobi-indan

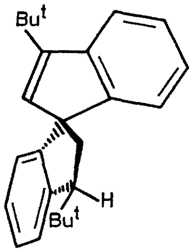
By SEIICHI IMAJO, ATSUMASA KATO, and KEIJI SHINGU*
(*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka* 560, *Japan*)

Summary A third diastereomer of 3,3′-di-t-butyl-1,1′-spirobi-indan, (1*S*, 3*R*, 3′*S*)-(**1c**), in addition to those prepared previously, has been prepared; its chiroptical behaviour in the ^1B and ^1L_a region was consistent with expectations based on the previously proposed exciton model for (**1a**) and (**1b**).

RECENTLY, we found that the two diastereomers of 3,3′-di-t-butyl-1,1′-spirobi-indan, (1*R*, 3*S*, 3′*S*)-(+)-(**1a**) and (1*S*,3*S*,3′*S*)-(+)-(**1b**), showed similar features in their c.d. spectra, irrespective of the mutually opposite configuration at the spiro centre.[1] The c.d. behaviour in the ^1B_b and ^1L_a region was explained on the basis of the coupling mode of the aromatic transition moments. However, since these two diastereomers have the same configuration at the 3- and 3′-position, this anomalous c.d. behaviour might be ascribed, at least in part, to the perturbation effect of the benzylic t-butyl group on each indan unit.[2] In order to resolve this ambiguity, we have synthesized another diastereomer, (1*S*,3*R*,3′*S*)-(+)-(**1c**), in which the configurations at these positions are opposite to each other. Thus all the three possible isomers of (**1**), as far as the relative configuration is concerned, have now been obtained in optically active form.



	R1	R2	R3	R4
(-)-(1a)	H	Bu^t	Bu^t	H
(+)-(1b)	Bu^t	H	H	Bu^t
(+)-(1c)	H	Bu^t	H	Bu^t
(-)-(2)	H	H	H	H
(+)-(3)	Me	Me	Me	Me



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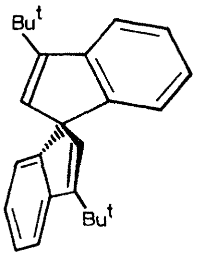

(5)

Dehydrogenation of (+)-(**1b**) with 1 mol of dichlorodicyanobenzoquinone gave a mixture of recovered (**1b**), the dihydrospirobi-indene (**4**), and a small amount of the spirobi-indene (**5**). Hydrogenation of this mixture with Adams catalyst afforded a diastereomeric mixture of (**1b**), (**1c**), and a small amount of (**1a**), which was separated by h.p.l.c. to give pure (1*S*,3*R*,3′*S*)-(+)-(**1c**) {$[\alpha]_{589}$ + 64·8° (iso-octane), m.p. 101·6—103·7 °C} [yield 26% from (+)-(**1b**)]. The formation of (+)-(**1c**) could be accounted for by the attack of hydrogen from the less hindered side of the indene unit of (1*S*,3*S*)-(**4**).†

N.m.r. data of (**1c**) showed that both the two five-membered rings are puckered in such a way that the t-butyl groups assume quasi-equatorial orientations, suggesting that the dihedral angle between the benzene planes is about 90°, *i.e.*, an intermediate value between those for (**1a**) and (**1b**).

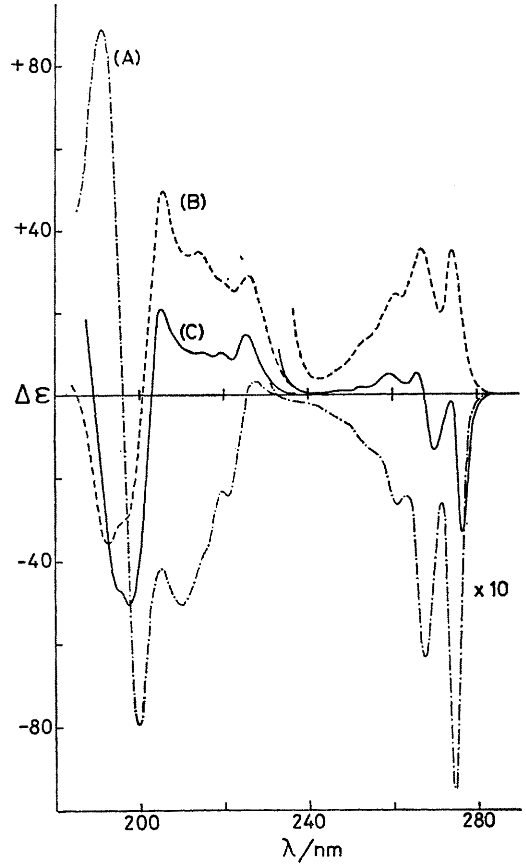

FIGURE 1. C.d. spectra of (A) (1*S*,3*R*,3′*R*)-(−)-(**1a**), (B) (1*S*,3*S*,3′*S*)(+)-(**1b**), and (C) (1*S*,3*R*,3′*S*)-(+)-(**1c**) in iso-octane.

Figure 1 depicts the c.d. spectra of the three diastereomers, (−)-(**1a**), (+)-(**1b**), and (+)-(**1c**), all of which have the (*S*) configuration at the spiro centre. In the ^1B region, the c.d. of (+)-(**1c**) is similar to that of (+)-(**1b**), but antipodal to that of (−)-(**1a**), while in the ^1L_a region all show a positive c.d. sign at the longest wavelength band.‡ Thus, considerations based on the spiro configuration alone[2,3a] are inadequate for the interpretation of the chiroptical properties of 1,1′-spirobi-indan, in spite of its relatively rigid structure. Instead, the observed c.d. behaviour of (**1c**) in the ^1L_a and ^1B region was in agreement with that predicted by the previously proposed exciton model[1] for (**1a**) and (**1b**), in which the ^1L_a moment is directed along the C(5)–C(8) axis and the ^1B_b moment perpendicular to that axis, since its lower frequency coupling modes for the ^1B_b and ^1L_a transition moments were found to be the same as those of (**1b**) (*A* and *B* symmetry, respectively), although (**1c**) does not rigorously belong to the point group C_2.§

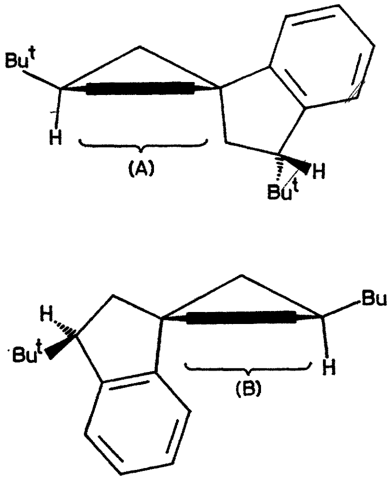

FIGURE 2. Disposition of substituents in each indan unit of (1*S*, 3*R*, 3′*S*)-(**1c**).

In the ^1L_b region, (**1c**) shows a bisignate[5] feature in contrast to (**1a**) and (**1b**).¶ This feature may be regarded as the overlap of c.d.s of opposite sign, each of which can be attributed to the individual indan unit perturbed by the substituents attached to it (see Figure 2). The contribution of each indan unit (A) and (B) could be estimated to be about half that of (**1a**) and (**1b**) (point group C_2), respect-

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† In another experiment, hydrogenation of (**5**) was found to afford exclusively (**1a**).

‡ The correspondence of the positive c.d. sign of the longest wavelength band in the ^1L_a region to the (*S*) spiro configuration is also found in the other 1,1′-spirobi-indans, (−)-(**2**) and (+)-(**3**) reported to date (refs. **3** and **4**). These compounds also show similar c.d. to (−)-(**1a**) in the ^1B and ^1L_b region.

§ The stable coupling mode of the ^1B_b moment is inverted from *B* symmetry for (**1a**) to *A* symmetry for (**1b**) and (**1c**), depending upon the dihedral angle between their benzene planes, while that of the ^1L_a moment is always of *B*-symmetry (see ref. 1).

¶ From the trends in the variation in the c.d. features among the three isomers, an interpretation based on the coupling mechanism, whether degenerate or nondegenerate, seemed to be inappropriate for the ^1L_b region (*cf.* ref. 1).

ively. The exact evaluation of the contribution of each substituent is difficult at present, but it may be assumed that the contribution of the benzene ring is dominant and that its sign is variable depending upon the orientation of the benzene ring (quasi-equatorial or quasi-axial), even if the spiro configuration is unchanged.

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