# Circular Dichroism of Diastereomeric 3,3′-Di-t-butyl-1,1′-spirobi-indans

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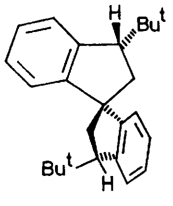
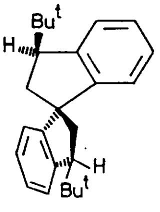
*Summary* Two diastereomeric 3,3′-di-t-butyl-1,1′-spirobi-indans, (1*R*,3*S*,3′*S*)-(**1a**) and (1*S*,3*S*,3′*S*)-(**1b**), have been prepared; their c.d. spectra are similar to each other in spite of the opposite configuration at the spiro centre.

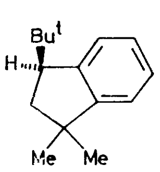
1,1′-SPIROBI-INDAN is an interesting compound in the study of chiroptical properties arising from the interaction between two benzene chromophores because of its relatively rigid geometry. From investigations so far of this compound,[1,2] the qualitative features of its c.d. spectra in the aromatic transition region seem to be characteristic of the configuration at the spiro centre and little affected by conformational changes in the molecule caused by puckering of the 5-membered ring.



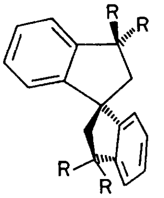
(1R,3S,3′S)-(+)-(1a)



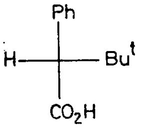
(1S,3S,3′S)-(+)-(1b)



(S)-(+)-(2)



(R)-(+)-(3); R = H
(R)-(−)-(4); R = Me



(S)-(+)-(5)

We have prepared two diastereomeric 3,3′-di-t-butyl-1,1′-spirobi-indans (1R,3S,3′S)-(+)-(**1a**) {$[\alpha]_D$ +131° (iso-octane), m.p. 168·2—169·6 °C} and (1S,3S,3′S)-(+)-(**1b**) {$[\alpha]_D$ +210° (iso-octane), m.p. 104·2—104·6 °C}, as well as the reference compound (S)-(+)-(**2**) {$[\alpha]_D$ + 8·7° (iso-octane), b.p. 100 °C (bath temp.) at 10 mmHg}† starting from (S)-(+)-t-butylphenylacetic acid (**5**).[3] The absolute configurations of (**1a**) and (**1b**) at the spiro centre were assigned on the basis of the relative configuration of the chiral centres in each isomer determined from their $^{1}$H n.m.r. spectra. The data showed that the 5-membered rings are puckered in such a way that the Bu$^t$ groups assume quasi-equatorial orientations, causing a large difference in the dihedral angle between the benzene ring planes in the two isomers {*ca.* 65 and 105° for (**1a**) and (**1b**), respectively}.‡

The u.v. and c.d. spectra of (+)-(**1a**) and (+)-(**1b**) are given in Figure 1 together with those of (+)-(**2**). In spite of the mutually opposite configuration at the spiro centre, (+)-(**1a**) and (+)-(**1b**) showed not only molecular rotations of the same sign and equal order of magnitude (+434 and +699°, respectively), but also similar features in the c.d. spectra, except for a minor difference in the $^{1}L_a$ region.

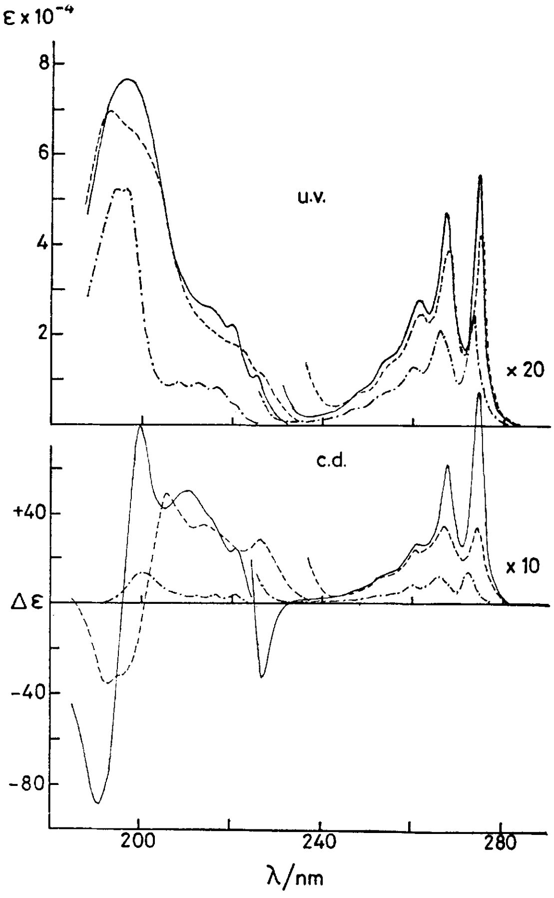


FIGURE 1. U.v. and c.d. spectra of (1R,3S,3′S)-(+)-(**1a**) (———), (1S,3S,3′S)-(+)-(**1b**) (-----), and (S)-(+)-(**2**) (-.-.-) in iso-octane.

In particular, strong couplets with the same sign were observed in the $^{1}B$ region. This behaviour cannot be attributed merely to the perturbation effect of the benzylic t-butyl groups, since (S)-(+)-(**2**) has a small $[M]_D$ value (+17·4°) and only positive c.d. for all absorption bands in the accessible region. Furthermore, (+)-(**1a**) shows the same c.d. sign as the known (R)-1,1′-spirobi-indans, (**3**)[2] and (**4**),[1c] in every absorption band, whilst (−)-(**1b**) which has the same spiro configuration must show a nearly antipodal pattern of c.d. spectra to these compounds. These facts indicate that the c.d. sign of 1,1′-spirobi-indan depends upon the conformation of the 5-membered rings, *i.e.*, on the relative disposition of the two benzene rings, at least in the $^{1}L_b$ and $^{1}B$ region.

We noted previously[1a,c] that the sign of couplet observed for (**4**) in the $^{1}L_a$ region was opposite to that expected on the basis of the exciton model,[4] when the direction of the local transition moment was assumed to be nearly perpendicular

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† All new compounds gave satisfactory elemental analyses and i.r. and n.m.r. spectra.

‡ X-ray diffraction study (Drs. H. Nakai and M. Shiro, Shionogi Research Laboratory) offered corroborating evidence for the conformation of (**1a**), whilst it was found in case of (**1b**) that one of the Bu$^t$ groups assumes a quasi-axial orientation so that the dihedral angle is *ca.* 90°. This, together with the n.m.r. data, seems to show a minute difference in strain energy between the two conformers of (**1b**) Details will be reported in the near future.

to the local $C_2$ axis of the aromatic ring by the use of Platt's spectroscopic moment.[5]§ The exciton model is now re-examined by directing the ${}^1L_a$ moment along the C(5)–C(8) axis and the ${}^1B_b$ moment perpendicular to that axis on the basis of a simple approximation that the polarization directions of these local transition moments are governed by the homoconjugation between C(8) and C(8′) (Figure 2).¶ Thus the lower-frequency coupling mode in the ${}^1L_a$ region should be of $B$ symmetry for both isomers, while that in the ${}^1B$ region should be of $B$ and $A$ symmetry for (**1a**) and (**1b**), respectively, reflecting the difference between them in the mutual disposition of the benzene ring.** Thus, the signs of the couplets observed for (+)-(**1a**) (negative in the ${}^1L_a$ and positive in the ${}^1B$ region) are in fair agreement with those expected. Similar consistency was observed for (+)-(**1b**) except that the higher-frequency side of the couplet in the ${}^1L_a$ region seems to be overlaid by the following c.d. with the opposite sign.

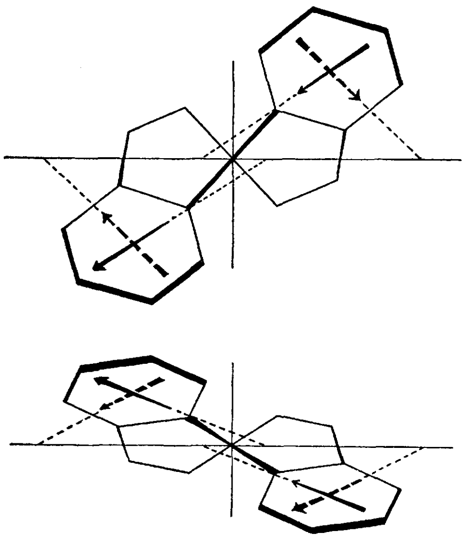

FIGURE 2. The lower-energy coupling mode of the ${}^1L_a$ (——>) and ${}^1B_b$ (----->) transition moments for (1$R$,3$S$,3′$S$)-(+)-(**1a**) (left) and (1$S$,3$S$,3′$S$)-(+)-(**1b**) (right).

The c.d. spectra observed for both isomers in the ${}^1L_b$ region are not explicable on the basis of the degenerate exciton model described above, since no coupling pattern is found in this region, as is often the case with other benzene chromophore dimers.[4,7] Moreover, quadrant sector rules[2a,8] or Snatske's modified rule[9] cannot consistently explain the observed c.d. sign which is positive for both isomers, if the predominant contribution of the confronting benzene ring is presupposed. This behaviour might be attributed to the non-degenerate coupling[10] of the ${}^1L_b$ transition moment of one benzene chromophore with the ${}^1B_b$ moment of the other, assuming that the two moments have nearly the same local direction.

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§ All the point transition dipoles were placed at the centre of the benzene rings and directed within the benzene plane according to Mason's procedure (ref. 4). A referee has pointed out the possibility that the direction of the transition moment deviates out of the plane of the benzene ring owing to perturbation by the Bu$^t$ group, as is found by linear dichroism for the $\lambda_2$ transition of steroidal olefins (A. Yogiv, J. Sagiv, and Y. Mazur, *J. Amer. Chem. Soc.*, 1972, **94**, 5122). However, we think such a deviation, if any, is very small for the aromatic $\pi \rightarrow \pi^*$ transition in view of work on aromatic steroids (ref. 6).

¶ Another component of the almost degenerate ${}^1B$ transition, namely, the ${}^1B_a$ moment which is directed perpendicular to the ${}^1B_b$ moment and has nearly equal magnitude to it, should be taken into account (ref. 6). However, the relative amplitudes of the c.d. couplet (P. M. Bayley, *Progr. Biophys. Mol. Biol.*, 1973, **27**, 1) calculated from the angular factor for the coupling between the two ${}^1B_a$ and between the ${}^1B_a$ of one benzene chromophore and the ${}^1B_b$ of the other were found, in both isomers, to be considerably smaller than those for the coupling between the two ${}^1B_b$, so that the contribution of the ${}^1B_a$ to the sign of the couplet was neglected.

** The coupling mode for (**1b**) was found to be the same in both the two conformers (see footnote ‡).

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