Conformational Dependence of Circular Dichroism of 1,1′-Spirobi[benz[*e*]indan]

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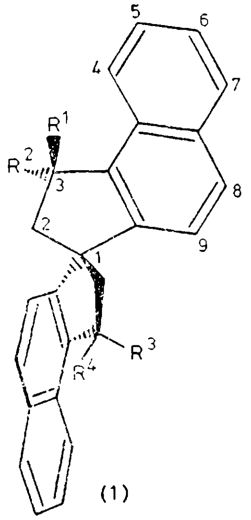
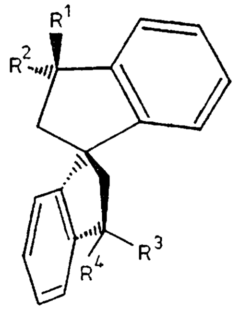
Summary Three diastereomers of 3,3′-di-t-butyl-1,1′-spirobi[benz[*e*]indan], (1*S*,3*R*,3′*R*)-(**1a**), (1*S*,3*S*,3′*S*)-(**1b**), and (1*S*,3*R*,3′*S*)-(**1c**), have been prepared; c.d. spectral evidence is presented for their different conformations.

Recently, we found that the c.d. spectra of the diastereomers of 3,3′-di-t-butyl-1,1′-spirobi-indan (**2a**—**c**) were dependent on the conformation caused by puckering of the five-membered rings, even if the configuration at the spiro centre was unchanged.[1] Thus 1,1′-spirobi-indans whose conformations are fixed by Bu^t groups have proved useful for systematic studies of the conformational dependence of c.d. spectra resulting from interaction between aromatic chromophores.



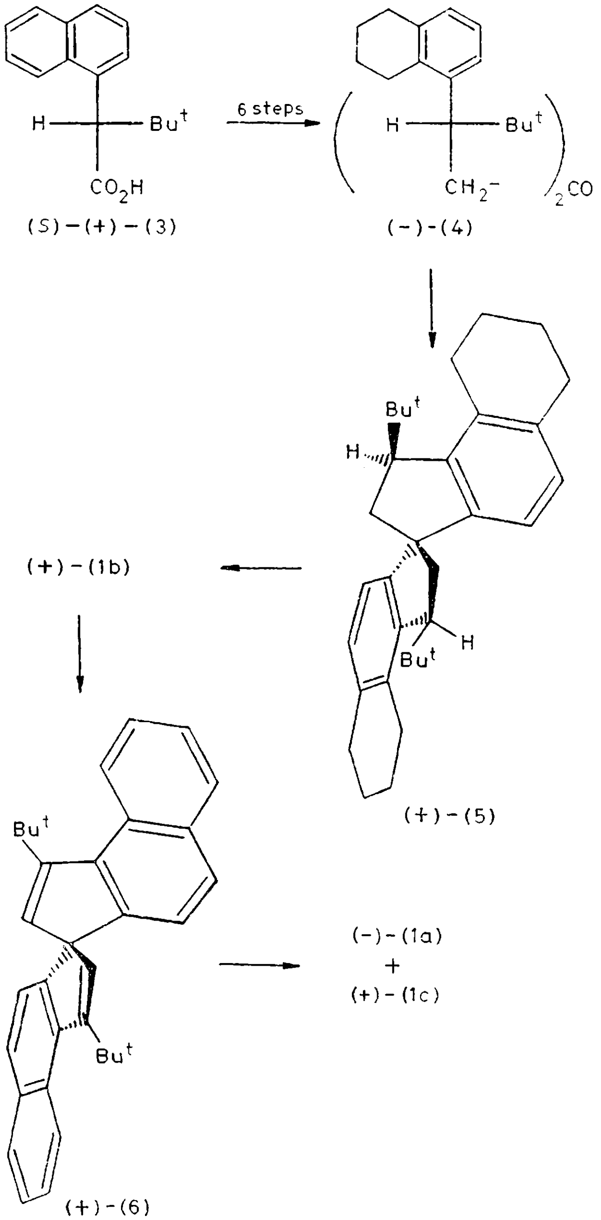
(1)



(2)

(−)-(**a**) R^1 = H, R^2 = R^3 = Bu^t, R^4 = H
(+)-(**b**) R^1 = Bu^t, R^2 = R^3 = H, R^4 = Bu^t
(+)-(**c**) R^1 = H, R^2 = Bu^t, R^3 = H, R^4 = Bu^t

Accordingly, we have now prepared three diastereomers of 3,3′-di-t-butyl-1,1′-spirobi[benz[*e*]indan], (1*S*,3*R*,3′*R*)-(−)-(**1a**) {$[\alpha]_{589}$ −48° (iso-octane), m.p. 245·6—246·6 °C}, (1*S*,3*S*,3′*S*)-(+)-(**1b**) {$[\alpha]_{589}$ + 505° (iso-octane), m.p. 285·5—286·4 °C}, and (1*S*,3*R*,3′*S*)-(+)-(**1c**) {$[\alpha]_{589}$ + 173° (iso-octane), m.p. 223·6—224·1 °C}, as the naphthalene chromophore is known to have transition moments with a distinct polarization direction and a large dipole strength in the near-u.v. region.[2]



Scheme

(−)-(**4**) {$[\alpha]_{589}$ −75·0° (ethanol), m.p. 100·0—101·6 °C}, prepared *via* several steps from (*S*)-(+)-α-t-butyl-α-naphthylacetic acid (**3**),[3] was cyclodehydrated by the action of phosphoric anhydride in methanesulphonic acid[4] to give exclusively (+)-(**5**) {$[\alpha]_{589}$ + 122° (iso-octane), m.p. 225·2—225·9 °C, yield 85%}† which was dehydrogenated

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† The high stereoselectivity in the cyclization reaction can be accounted for by the steric effects of the Bu^t group buttressed by the benzylic methylene group of the tetralin skeleton, and may enable the assignment of the *rel*-(1*S*,3*S*,3′*S*)-configuration to (**1b**). This assignment was supported by n.m.r. data.

with dichlorodicyanobenzoquinone to yield (+)-(**1b**). Dehydrogenation of (**1b**) with *N*-bromosuccinimide afforded the spirobi[benz[*e*]indene] (+)-(**6**) {$[\alpha]_{589}$ + 174° (iso-octane), m.p. 227 °C (decomp.)} which was hydrogenated with Pd—C to give a diastereomeric mixture (separated by h.p.l.c.) of (−)-(**1a**) and (+)-(**1c**) in the ratio 1:2 together with a trace of (+)-(**1b**) (Scheme).

The absolute configurations of (**1a**—**c**) were assigned on the basis of the relative configuration of chiral centres in each isomer determined from their ^{1}H n.m.r. spectra. The observed coupling constants between the methine and methylene protons indicated that the five-membered rings in (**1a**) and (**1c**) are puckered in such a way that the Bu^t groups assume quasi-equatorial orientations, but that those in (**1b**) are nearly planar. The extent of puckering was found to be smaller for these isomers than for the corresponding isomers of (**2**)[1] owing probably to steric repulsion between the Bu^t group and the hydrogen atom at the 4- or 4′-position. The estimated dihedral angles between two aromatic planes were *ca.* 75° for (**1a**) and *ca.* 90° for both (**1b**) and (**1c**), the difference between the latter two being obscure.‡

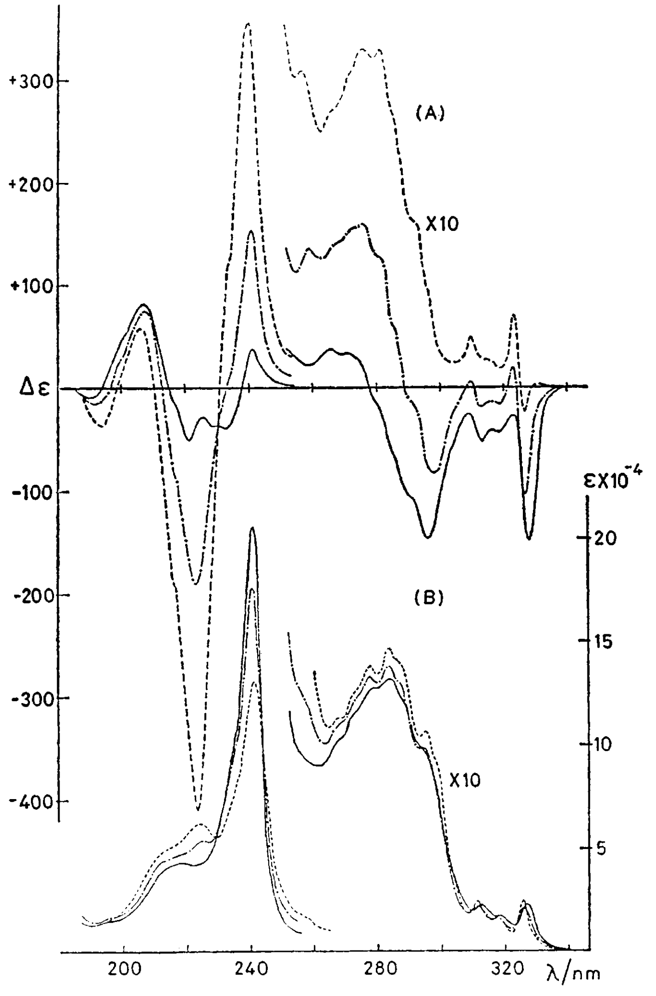

FIGURE 1. C.d. (A) and u.v. (B) spectra of (1*S*,3*R*,3′*R*)-(−)-(**1a**) (——), (1*S*,3*S*,3′*S*)-(+)-(**1b**) (- - - - -), and (1*S*,3*R*,3′*S*)-(+)-(**1c**) (- · - · - · -) in iso-octane.

The u.v. and c.d. spectra of (−)-(**1a**), (+)-(**1b**), and (+)-(**1c**) are shown in Figure 1. Large differences in the c.d. spectra of the three isomers were observed in spite of relatively small differences in the orientation of their naphthalene chromophores. In particular, the positive couplets in the ^{1}B$_b$ region differ greatly in amplitude, demonstrating the sensitivity of c.d. spectra to minute changes in conformation.§ We examined this c.d. behaviour on the basis of the exciton model in which the transition point-dipoles are located at the centres of the naphthalene rings[5] (Figure 2).

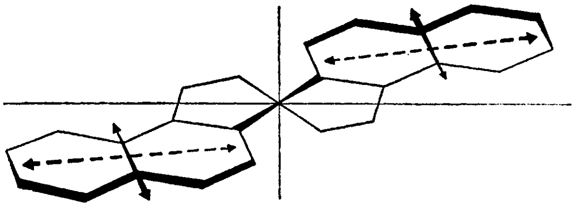

FIGURE 2. The polarisation directions of the ^{1}B$_b$ (←- - - - -→) and ^{1}L$_a$ (←——→) transitions of 1,1′-spirobi[benz[*e*]indan].

For the ^{1}B$_b$ transition in which the local moments are polarized along the long axes of the naphthalene rings, the lower-frequency coupling mode was calculated to be of *B* symmetry for all isomers, and the magnitude of splitting energy (V_{ij}, *ca.* 1800 cm^{-1}) varied little with conformation. However, the rotational strength was calculated to be sensitive to the change in conformation. It is nearly zero when the dihedral angle between the aromatic planes is small, since then the two point-dipoles are directed almost parallel to each other, but it increases rapidly as the dihedral angle becomes larger.¶ In fact, the amplitude of the couplet observed in the ^{1}B$_b$ region was found to increase steeply in the order (**1a**), (**1c**), and (**1b**), and the signs of the couplets were as expected from the absolute configurations. Thus it has been shown from c.d. spectra that (**1b**) has a larger dihedral angle than (**1c**), at least in solution.

For the ^{1}L$_a$ transition in which the local moments are polarized along the short axes of the naphthalene rings, the lower-frequency coupling mode was calculated to be inverted from *B* to *A* symmetry with the increase in the dihedral angle, the splitting energy being zero at *ca.* 90°. However, the rotational strength was found to change little

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‡ An *X*-ray diffraction study of these compounds is now in progress (Drs. H. Nakai and M. Shiro, Shionogi Research Laboratory).

§ It should be emphasized that typical patterns of exciton splitting and distinct differences between them are also observed in the u.v. spectra. The sharp peaks at *ca.* 240 nm and the weak bands at *ca.* 225 nm correspond, respectively, to *B*- and *A*-coupling of the ^1B_b transition [Δν, 2960 cm^{-1} for (**1b**)]. In (**1a**) the latter band is completely overlaid by a broad band at *ca.* 215 nm which is attributed to the ^{1}C$_b$ transition (ref. 2) and is also found in the c.d. spectra as the positive c.d. at *ca.* 208 nm. The calculated dipole strengths of the *A*-coupling of the ^{1}B$_b$ transition were *ca.* 0·6 and 4% of those of the *B*-coupling for (**1a**) and (**1b**), respectively, which was compatible with the observed spectra.

¶ (**1c**) does not rigorously belong to the point group C_2. The calculated rotational strength for a certain dihedral angle varies, depending upon the mode of the torsion of the five-membered rings, *viz.*, C_2 or non-C_2 symmetry. However, the difference between the two modes was found to be relatively small.

with conformation. The negative couplets observed for (**1a**) and (**1c**) and the non-couplet feature observed for (**1b**) were compatible with this. The positive c.d. of (**1b**) may be attributed to the non-degenerate coupling[5b,6] of the ^1L_a moment in one naphthalene chromophore with the ^1B_b moment in the other.**

We thank Drs. K. Kuriyama and M. Shiro, Shionogi Research Laboratory, for helpful suggestions.

(*Received, 25th May* 1979; *Com.* 552.)

** The c.d. spectra in the ^1L_b region are too complicated to be explained on the basis of the coupling mechanism. However, as was previously described for the compounds (**2**) (ref. 1b), the behaviour of (**1c**) may be regarded as an overlap of the features of (**1a**) and (**1b**), showing a regular dependence of the c.d. spectra in this region upon conformation.

[1] (a) S. Imajo, A. Kato, and K. Shingu, *J.C.S. Chem. Comm.*, 1978, 810; (b) *ibid.*, 1979, 25.

[2] H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, 1949, **17**, 470.

[3] H. Kuritani, S. Imajo, K. Shingu, and M. Nakagawa, *Tetrahedron Letters*, 1979, 1697; S. Imajo, H. Kuritani, K. Shingu, and M. Nakagawa, *J. Org. Chem.*, in the press.

[4] P. E. Eaton, G. R. Carlson, and J. T. Lee, *J. Org. Chem.*, 1973, **38**, 4071.

[5] Studies of exciton coupling between naphthalene chromophores have been made of dibenzethanoanthracenes and 1,1′-binaphthyls; (a) S. Hagishita and K. Kuriyama, *Tetrahedron*, 1972, **28**, 1435; (b) S. F. Mason, R. H. Seal, and D. R. Roberts, *ibid.*, 1974, **30**, 1671; (c) N. Harada, Y. Takuma, and H. Uda, *J. Amer. Chem. Soc.*, 1978, **100**, 4029.

[6] I. Tinoco, in 'Advances in Chemical Physics', ed. Prigogine, Interscience, New York, 1962, Vol. 4, p. 113; J. A. Schellman, *Accounts Chem. Res.*, 1968, **1**, 44.