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ABSOLUTE CONFIGURATION AND CONFORMATION OF 1,1'-SPIROBI[BENZ[*f*]INDAN]

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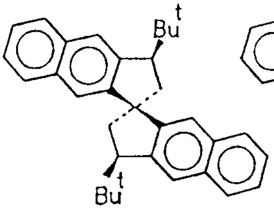
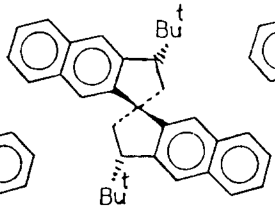
Summary: Three diastereomers of (1*S*)-3,3'-di-t-butyl-1,1'-spirobi[benz[*f*]indan] have been prepared. In the ^1B_b region all the isomers showed typical c.d. couplets of negative sign, reflecting the identity of configuration at the spiro center irrespective of their different conformations.

Recently, we found that the c.d. spectra of the diastereomers of 3,3'-di-*t*-butyl-1,1'-spirobi[benz[*e*]indan]2) and 3,3'-di-*t*-butyl-1,1'-spirobi[benz[*g*]-indan]3) were markedly influenced by the conformation of each, even if the configuration at the spiro center was unchanged. For further investigation of c.d. spectra resulting from interaction between aromatic chromophores, we have now prepared three diastereomers of 3,3'-di-*t*-butyl-1,1'-spirobi[benz[*f*]indan], (1*S*,3*R*,3'*R*)-(-)-**1a**, $[\alpha]_D$ -389° (isooctane), mp 274.3-276.4 °C, (1*S*,3*S*,3'*S*)-(-)-**1b**, $[\alpha]_D$ -200° (isooctane), mp 234.3-235.3 °C, and (1*S*,3*R*,3'*S*)-(-)-**1c**, $[\alpha]_D$ -225° (isooctane), mp 252.2-254.6 °C, having the third type of array of naphthalene chromophores.

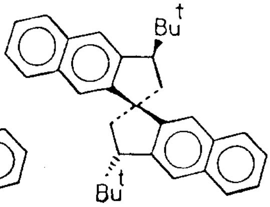
The octahydro-ketone (-)-**3**, $[\alpha]_D$ -58.4° (isooctane), mp 109.1-111.6 °C, prepared *via* several steps from (*S*)-(+)-*t*-butyl-β-naphthylacetic acid **2**3,4) was cyclodehydrated by the action of phosphoric anhydride in methanesulphonic acid



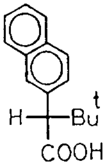
(1S,3R,3'R)-(-)-**1a**



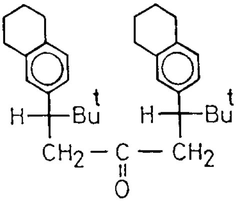
(1S,3S,3'S)-(-)-**1b**



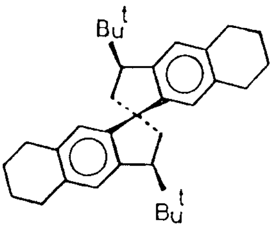
(1S,3R,3'S)-(-)-**1c**



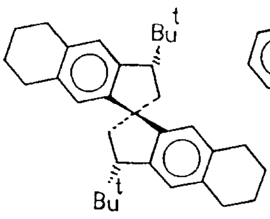
(S)-(+)-**2**



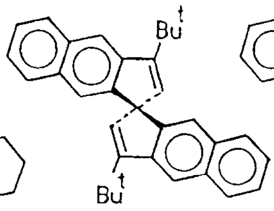
(3S,7S)-(-)-**3**



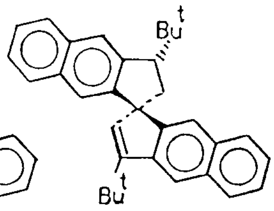
(1R,3S,3'S)-(+)-**4a**



(1S,3S,3'S)-(+)-**4b**



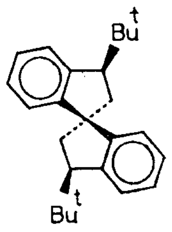
(1S)-(-)-**5**



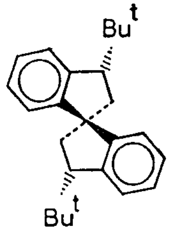
(1S,3S)-**6**

to give a diastereomeric mixture (separated by fractional crystallization and HPLC) of (+)-**4a**, $[\alpha]_D$ +152° (isooctane), mp 283.3-283.7 °C, and (+)-**4b**, $[\alpha]_D$ +56.7° (isooctane), mp 234.6-235.4 °C, in the ratio 9:2 (yield 61%).[5] ^{1}H-n.m.r. spectra of **4a** (H_9 δ 6.69, H_4 δ 7.18, each s) and **4b** (H_9 δ 6.57, H_4 δ 7.10, each s) clearly showed that they are C_2 compounds composed of two 1,2,4,5-tetrasubstituted benzene rings. Dehydrogenation of (+)-**4a** with large excess amount of DDQ gave the spirobi[benz[*f*]indene] (+)-**5**, $[\alpha]_D$ +1085° (isooctane), mp 195.9-196.9 °C. (+)-**4b** was dehydrogenated with 4 mols of DDQ, affording a mixture (separated by HPLC) of (-)-**1b**, (-)-**5**, and the dihydrospirobi[benzindene] **6**. Hydrogenation of (-)-**5** and **6** with Pd on carbon yielded (-)-**1a** and (-)-**1c**, respectively.

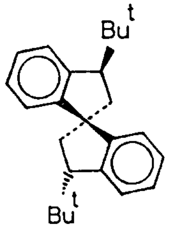
The absolute configurations of (-)-**1a**, (-)-**1b** and (-)-**1c** at the spiro center were assigned on the basis of the relative configurations of chiral centers in **1a** and **1b** (*trans-trans* and *cis-cis*, respectively) determined by comparison of n.m.r. spectra with each other, as well as configurationally defined spirobiindans, **7a** and **7b**[6,7] (Table). The observed coupling constants between the methine and methylene protons indicated that the corresponding diastereomers of **1** and **7** have similar extent of puckering of five-membered rings and, consequently, similar dihedral angles between aromatic planes. The angles are roughly estimated at *ca*. 65°, 105° and 90° for **a**, **b** and **c**, respectively.



(1S,3R,3'R)-(-)-**7a**



(1S,3S,3'S)-(-)-**7b**



(1S,3R,3'S)-(-)-**7c**

	chemical shift (δ)			coupling constant (Hz)		
	H_A	H_B or H_M	H_X	J_{AB} or J_{AM}	J_{AX}	J_{BX} or J_{MX}
1a	1.87	2.48	3.41	12.2	11.2	7.0
1b	2.86	2.32	3.69	13.5	8.8	8.2
1c	2.16	2.28	3.46	12.7	11.2	7.1
	2.65	2.33	3.48	11.9	11.9	6.9
7a	1.70	2.32	3.23	12.5	10.8	7.0
7b	2.65	2.15	3.40	13.8	9.0	7.8
7c	2.08	2.13	3.23	12.8	9.9	7.3
	2.39	2.21	3.30	12.2	11.2	6.8

Table. 100 MHz n.m.r. data for methine(H_X) and methylene protons (H_A; trans to H_X, and H_M; cis to H_X) of spirobi[benz[*f*]indan] (**1a**,**b**,**c**) and spirobiindan (**7a**,**b**,**c**) in $CDCl_3$.

Figure 1 shows the u.v. and c.d. spectra of (-)-1a, (-)-1b and (-)-1c, all of which have the (*S*)-configuration at the spiro center. The u.v. spectra of the three isomers closely resembled each other, all showing distinct exciton splitting in the ^1B_b region. Comparison of the positions of peaks in the u.v. spectra with those in the c.d. spectra gave good agreement in that region. The amplitude of c.d. couplet, not to mention its sign, was virtually invariant, in contrast to the behavior of other types of 1,1'-spirobi[benzindan]s$^{2,3)}$ and the parent compound 7.$^{6)}$ Thus, in this type of spirobi[benzindan], the couplet feature resulting from the interaction between the ^1B_b moments of naphthalene chromophores was found to be insensitive to the change in conformation, and hence to be readily accessible for the determination of the absolute configuration at the spiro center. We examined this c.d. behavior on the basis of the exciton model in which the transition point-dipoles are located at the centers of naphthalene rings (Figure 2).

For the ^1B_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 splitting energy (*ca.*

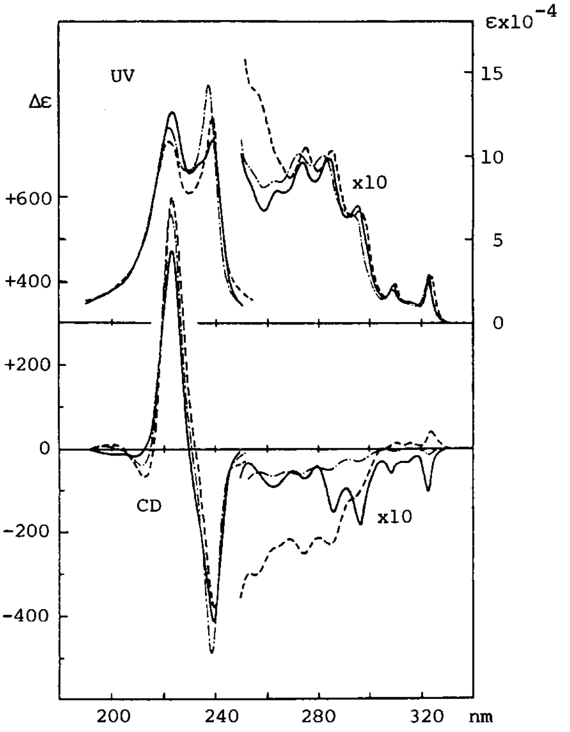


Figure 1. U.v. and c.d. spectra of (1S,3R,3'R)-(-)-1a (———), (1S,3S,3'S)-(-)-1b (- - - -) and (1S,3R,3'S)-(-)-1c (—·—·—) in isooctane.

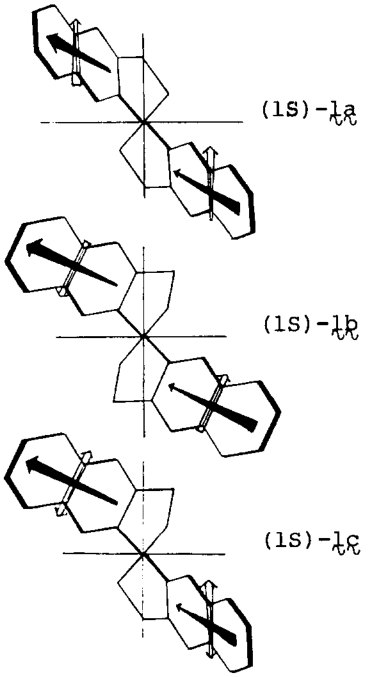


Figure 2. The lower frequency coupling mode of ^1B_b (black arrow) and ^1L_a (white arrow) transitions in 1 (the splitting energy of the ^1L_a is nearly zero for 1c).

1900 cm^{-1}) varied little with conformation. Furthermore, the calculated rotational strength ($-1.02 \sim -1.29 \times 10^{-37}$ c.g.s. for B-coupling) was insensitive to the change in conformation. The negative c.d. couplets with similar amplitudes observed for the three isomers are consistent with the results of calculation. Thus, owing to the appropriate orientation of local ^1B_b transitions, 1,1'-spirobi[benz[*f*]indan] has proved to offer an apt illustration of the C_2-rule.[8,9] Its chirality of chromophore (left-handed for the (1*S*)-configuration) can easily be seen from Figure 2.

On the other hand, the c.d. spectra in the ^1L_a region showed no couplet pattern for these isomers except that the short wavelength side of the couplet expectable for **1a** seemed to be overlaid by the following c.d. with the opposite sign. According to the exciton theory, the lower-frequency coupling mode of the local moments polarized along the short axes of the naphthalene rings was calculated to be inverted from B to A symmetry (V_B, *ca.* $-140 \sim +110$ cm^{-1}) with the increase in the dihedral angle, the splitting energy being nearly zero for **1c** (Figure 2). Almost the same result was obtained by calculating the repulsion between the transition monopoles[10] using the HMO coefficients of naphthalene. In addition, the two point-dipoles of **1b** are directed almost parallel to each other, and the ^1L_a transition of naphthalene itself, though electrically allowed, has a relatively small dipole strength ($D \simeq 1 \times 10^{-35}$). Therefore, the non-couplet features observed for these isomers in the ^1L_a region, unlike other types of 1,1'-spirobibenzindans,[2,3] could be attributed to some perturbation effect exceeding the minor contribution of the coupling mechanism.[11]

References and Notes

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4) O. Piccolo, R. Menicagli, and L. Lardicci, *Tetrahedron*, 35, 1751 (1979).
5) The regioselectivity of the cyclization reaction was ensured by the pre-hydrogenation of the naphthalene nuclei to tetralin skeletons.
6) S. Imajo, A. Kato, and K. Shingu, *J. C. S. Chem. Comm.*, 810 (1978); 25 (1979).
7) This assignment was corroborated by a direct chemical correlation of (-)-**1a** with configurationally established (-)-**7a**. Details will be reported elsewhere.
8) G. Wagnière and W. Hug, *Tetrahedron Lett.*, 4763 (1970); W. Hug and G. Wagnière, *Tetrahedron*, 28, 1241 (1972).
9) **1c** does not rigorously belong to the point group C_2. The rotational strength and splitting energy for a given dihedral angle were calculated to change, depending upon the puckering mode, *viz.*, C_2 or non-C_2 symmetry. However, the difference between the two modes was found to be small.
10) S. F. Mason, in "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," ed. G. Snatzke, Heyden and Son, London, 1967, p.71.
11) The c.d. features in the ^1L_b region showed a regular dependence upon conformation similar to those for other types of 1,1'-spirobi[benzindan]s and 1,1'-spirobiindan (ref. 2,3,6).

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