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

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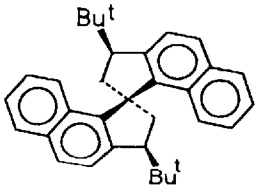
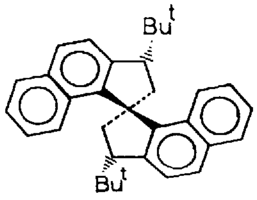
Summary: Two diastereomers of 3,3'-di-*t*-butyl-1,1'-spirobi[benz[*g*]indan] have been prepared; c.d. spectral evidence is presented for the difference between their conformations.

Recently, we found that the c.d. spectra of three diastereomers of 3,3'-di-*t*-butyl-1,1'-spirobi[benz[*e*]indan] were markedly dependent upon the conformation of each, even if the configuration at the spiro center was unchanged.$^{1)}$ Thus 1,1'-spirobi[benzindan]s have proved useful for systematic studies of the conformation dependence of c.d. spectra arising from the interaction between aromatic chromophores, on account of the distinct polarization direction and large dipole strength of the transition moments of naphthalene chromophores. To inquire into the c.d. behavior of another type of array of naphthalene chromophores, we have now prepared two diastereomers of 3,3'-di-*t*-butyl-1,1'-spirobi[benz[*g*]indan], (*1R,3S,3'S*)-(−)-**1a** and (*1S,3S,3'S*)-(+)-**1b**, both having C_2 symmetry.

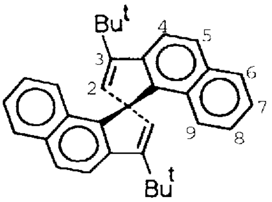
The ketone (−)-**3**, $[\alpha]_D$ −208° (benzene), mp 148.2-149.5 °C, prepared via several steps from (*S*)-(+)-*t*-butyl-β-naphthylacetic acid **4**,$^{2)}$ $[\alpha]_D$ +30.6° (benzene), mp 187.4-188.6 °C, was cyclodehydrated by the action of phosphoric anhydride in methanesulphonic acid to give a diastereomeric mixture (separated by



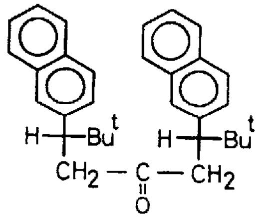
(1R,3S,3'S)-(−)-**1a**



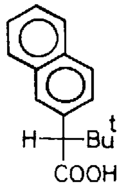
(1S,3S,3'S)-(+)-**1b**



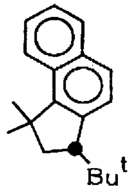
(R)-(+)-**2**



(3S,7S)-(−)-**3**



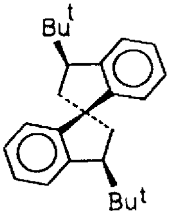
(S)-(+)-**4**



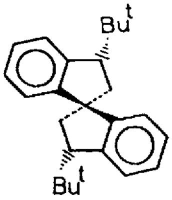
(S)-(−)-**5**

column chromatography on silica gel) of (-)-**1a**, $[\alpha]_D$ -29.6° (isooctane), mp 159.0-160.7 °C, and (+)-**1b**, $[\alpha]_D$ +275° (isooctane), mp 291.3-292.5 °C, in the ratio 5:2 (yield 75%). Dehydrogenation of (-)-**1a** and (+)-**1b** with NBS, followed by reduction with LAH to remove vinylic bromine, afforded spirobi[benz[*g*]indene], (+)-**2**, $[\alpha]_D$ +352° (isooctane), mp 220 °C (dec.), and (-)-**2**, respectively, proving that the former two have mutually opposite configurations at the spiro center. The reference compound (*S*)-(-)-**5**, $[\alpha]_D$ -2.2°, $[\alpha]_{405}$ +34.6° (isooctane), mp 111.1-113.1 °C, was prepared from (+)-**4** via a similar route.

^1H n.m.r. spectrum of **2** (H_4 δ 7.97, H_5 δ 7.84, J_{45} 8.5 Hz; H_6 δ 7.67, H_7 δ 7.17, H_8 δ 6.99, H_9 δ 6.75, J_{67} 8.1, J_{78} 1.4, J_{79} 1.5, J_{89} 8.4 Hz) clearly showed that **2** and, consequently, **1a** and **1b** are C_2 compounds composed of two 1,2-disubstituted naphthalene rings. Furthermore, the absolute configurations of **1a** and **1b** were assigned on the basis of the relative configuration of chiral centers in each isomer (*trans,trans* and *cis,cis*, respectively) determined by comparison of ^1H n.m.r. spectra with each other and with **5**, as well as with configurationally defined spirobiindans (**6a** and **6b**)$^{3)}$ (Table). The observed coupling constants indicated that the five-membered rings are puckered in such a way that the *t*-butyl groups assume quasi-equatorial orientations. The dihedral angles between two aromatic planes were roughly estimated at ca. 60° for **1a** and ca. 110° for **1b** from the torsional angles around the C_2-C_3 bond calculated according to the modified Karplus equation.$^{5,6)}$



(1R,3S,3'S)-(+)-**6a**



(1S,3S,3'S)-(+)-**6b**

Figure 1 and 2 depict, respectively, the u.v. and c.d. spectra of (*1S*,*3R*,*3'R*)-(+)-**1a** and (*1S*,*3S*,*3'S*)-(+)-**1b** with the same spiro-configuration, and those of the reference compound (*S*)-(-)-**5**. The u.v. spectra of the two

Table. N.m.r. data for methine (H_X) and methylene protons (H_A; trans to H_X, and H_B or H_M; cis to H_X) of benz[*g*]indan **5**, spirobi[benz[*g*]-indan] **1a**, **1b**, and spirobiindan **6a**, **6b** in $CDCl_3$.

	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	2.11	2.44	3.41	12.8	11.9	6.7
1b	3.11	2.54	3.61	14.7	10.6	3.7$^{4)}$
5	1.88	2.08	3.19	12.8	10.0	8.0
6a	1.70	2.32	3.23	12.5	10.8	7.0
6b	2.65	2.15	3.40	13.8	9.0	7.8

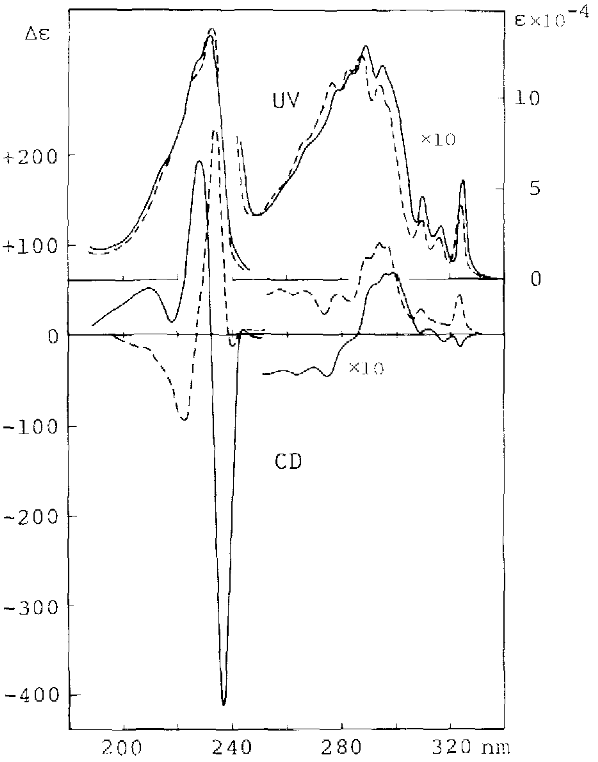


Figure 1. U.v. and c.d. spectra of (*1S,3R,3'R*)-(+)-**1a** (———) and (*1S,3S,3'S*)-(+)-**1b** (-----) in isooctane.

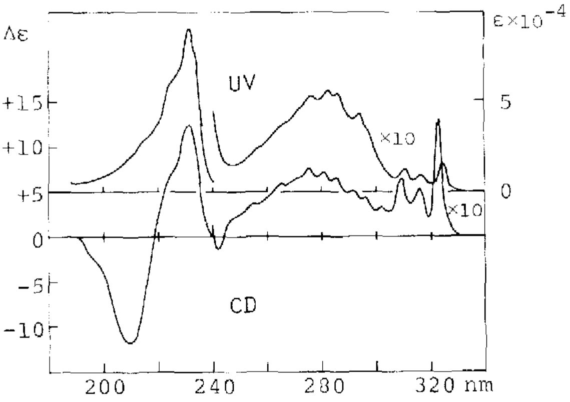


Figure 2. U.v. and c.d. spectra of (*S*)-(−)-**5** in isooctane.

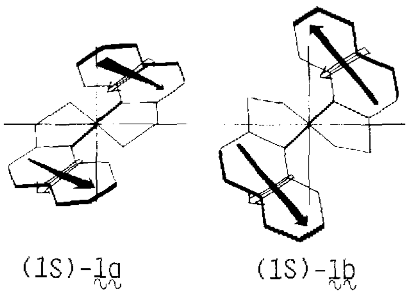


Figure 3. The lower frequency coupling mode of ^1B_b (black arrow) and ^1L_a (white arrow) transitions in **1a** and **1b**.

isomers (+)-**1a** and (+)-**1b** closely resemble each other in every region, not showing such a large exciton splitting in the ^1B_b region as was observed for spirobi[benz[*e*]indan]s.$^{1)}$ However, a distinct difference was found in the c.d. spectra; thus, the couplets in the ^1B_b region showed antipodal features to each other in spite of the same configuration at the spiro center. This fact offers an additional illustration of seemingly anomalous c.d. behavior which has already been observed for **6a** and **6b** in the doubly degenerate ^1B region.$^{3)}$ It is worth noting that a relatively small change in conformation may cause such a behavior which is in conflict with the C_2-rule,$^{7)}$ if the lower-energy coupling mode of ^1B_b transition moments is assumed to be unchanged.

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 (see Figure 3). 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 A-symmetry for most of the possible conformations, but the mode proved to be inverted to B-symmetry with the decrease in the dihedral angle between two aromatic planes, the splitting energy being zero at ca. 68°.8) Hence the signs of couplets observed for **1a** and **1b** were in accord with the expectations from the assigned configurations and conformations.

For the ^1L_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 of B-symmetry in any conformation. The positive couplets observed for **1a** and **1b** are compatible with this, though, in the latter, the higher-frequency side of the couplet seems to be overlaid by the following c.d. with opposite sign.9,10)

The positive and negative c.d. observed respectively for **1a** and **1b** at ca. 210 nm could be attributed to the ^1C_b transition, which was also observed in the c.d. spectrum of **5**. In the u.v. spectra, this band is obscured by the ^1B_b, since the $^1C_b \leftarrow {}^1A$ transitions are electrically forbidden in the acene molecules.11)

References and Notes

1) S. Imajo, A. Nakamura, K. Shingu, A. Kato, and M. Nakagawa, *J. C. S. Chem. Comm.*, 868(1979).
2) Successful resolution of **4** was achieved via quinine salt. Its absolute configuration has recently been determined by Menicagli et al.; O. Piccolo, R. Menicagli, and L. Lardicci, *Tetrahedron*, 35, 1751 (1979).
3) S. Imajo, A. Kato, and K. Shingu, *J. C. S. Chem. Comm.*, 810 (1978); 25 (1979)
4) The C_3-H_X bond in **1b** is possibly bent to such a direction that H_X moves away from H_M to reduce the steric repulsion between H_X and the confronting aromatic proton $H_{9'}$.
5) R. J. Abraham and W. A. Thomas, *J. Chem. Soc.*, 3739 (1964). The large downfield shifts of H_As in **1b** and **6b** possibly due to the effect of steric compression are sufficient for the distinction between diastereomeric configurations. However, some uncertainty in the accuracy of the calculated torsional angles is unavoidable, and, in the present work, the analyses of c.d. spectra seem to offer more definite evidence for the conformation in solution
6) X-ray diffraction study (Drs. H. Nakai and M. Shiro, Shionogi Research Laboratory) has offered corroborating evidence for this assignment of diastereomeric configurations. However, the dihedral angles between aromatic planes were found to be 84° and 88° for **1a** and **1b**, respectively, in the crystalline state. This fact seems to show minute differences in strain energy between the conformers of 1,1'-spirobi[benz[*g*]indan].
7) W. Hug and G. Wagniere, *Tetrahedron*, 28, 1241 (1972).
8) The same result was obtained by calculating the repulsion between the transition monopoles using the HMO coefficients of naphthalene, though, in every conformation, the magnitude of splitting energy was somewhat smaller than that calculated by the exciton method. On the contrary, calculation based on the molecular structure given by X-ray analyses predicted that the lower-frequency coupling modes were of A-symmetry for both **1a** and **1b**.
9) The origin of the weak c.d. absorptions at ca. 240-260 nm, oppositely signed to each other for two isomers, is difficult to assign at present. However, it should be noted that a similar c.d. was also observed for **5**.
10) The c.d. signs of **1a** and **1b** with the same spiro-configuration were opposite to each other in the ^1L_b region, as was observed previously in the case of **6a** and **6b** (ref. 3).
11) J. R. Platt, *J. Chem. Phys.*, 17, 484 (1949).

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