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EFFECT OF SPIROCONJUGATION ON THE UV AND CD SPECTRA OF 1,1'-SPIROBIINDENE

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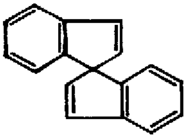
Summary: U.v. and c.d. spectra of 1,1'-spirobiindene were theoretically explained based on the composite molecule method. The effect of spiroconjugation was shown to appear markedly in the ^1L_a region of indene, making a large splitting of this band, as was expected from PE spectra.

Since the proposal of the concept of spiroconjugation1) which describes the interaction of two π-systems separated by an insulating tetrahedral center, many attempted syntheses and theoretical discussions about spiroconjugated systems have been appeared in the literature.2) Spiro[4.4]nonatetraene (1), one of the most typical model compounds of spiroconjugation, has been reported to show the predicted behavior in both electronic and photoelectron spectra.2b) Spirobiindene (2) has also been proved to exhibit spiroconjugation effect in photoelectron spectra,2c) yet its electronic spectra has not been analysed theoretically, although a remarkable contrast to its monomeric component, indene, has been noticed.3)

For the evaluation of spiroconjugation effect on u.v. and c.d. spectra, we have prepared (*S*)-(-)-3,3'-di-*t*-butyl-1,1'-spirobiindene (3), $[\alpha]_{589}$ -214° (isooctane), mp 209.7∿210.8 °C, by the dehydrogenation of (*1S*,*3R*,*3'R*)-(-)-3.3'-di-*t*-butyl-1,1'-spirobiindan (4)4) with DDQ. The reference monomeric compound, 1,1-dimethyl-3-*t*-butylindene (5), mp 47∿48 °C, was also obtained from 1,1-dimethyl-3-*t*-butylindan (6)4) by the same procedure.


1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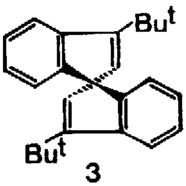
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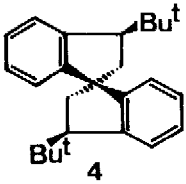
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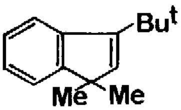
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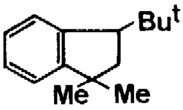
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The u.v. and c.d. spectra of 3 are shown in Figure 1 together with the u.v. of 5. At a glance, 3 seems to show merely a bathochromic shift compared with 5, as has already been pointed out for 2.3) However, in spite of the presence of two indene chromophores, 3 shows a band at ca. 275 nm whose intensity is too low to be assigned to a normal ^1L_a transition. Furthermore, the wavelength difference between the absorptions at ca. 275 and 235 nm is too large (ca. 6000 cm^{-1}) to be attributed to a simple exciton splitting of the two local ^1L_a transitions. Thus the u.v.

spectra of 3 is a striking contrast to that of 1,1'-spirobiindan 4 which is closely similar to its reference compound 6, having approximately twice the intensity of 6, and showing little homoconjugation effects.4) Moreover, c.d. spectra of 3 is too complicated to be explained by a simple exciton coupling at any region.

For the quantitative estimation of the effect of spiroconjugation on u.v. and c.d. spectra, the electronic state of 1,1'-spirobiindene was calculated by the use of composite molecule method (Longuet-Higgins-Murrell formalism5)) which has been recognized very useful in taking into accout the conjugation effect and in clarifying the nature and origin of the coupling between chromophores. Thus, 1,1'-spirobiindene was regarded to be made up of two indene chromophores, and the electronic states of local chromophore obtained by the π-SCF-MO-CI formalism of Pariser-Parr-Pople method6) were used. The allowed excited states of indene taken into account were, from lower to higher energy level, ^1L_a, ^1B_b and ^1B_a ones whose transition moments given by dipole velocity method using the reported $\vec{\nabla}_{rs}$ integrals7) are shown in Table 1. The resulting polarization directions of the three states are in accord with those generally accepted.

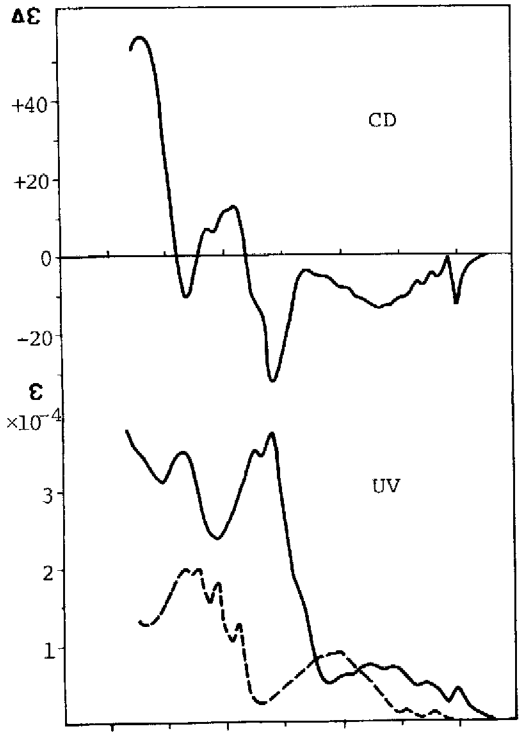


Figure 1. The u.v. and c.d. spectra of (S)-(-)-3 (———) and u.v. spectrum of 5 (-----) in isooctane.

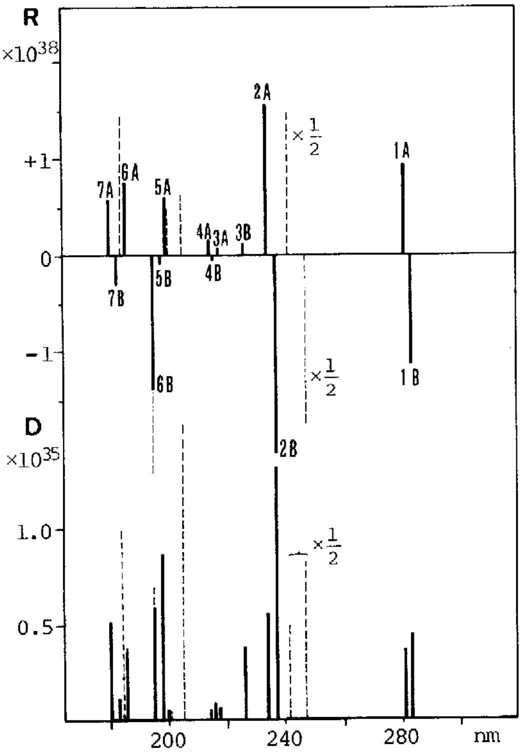
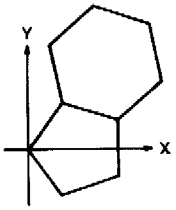


Figure 2. The calculated rotational (upper) and dipole (lower) strengths for (S)-spirobiindene. Broken lines show those for the case $\beta_{spiro} = 0$.

For the calculation of spirobiindene, nineteen electronic states were considered, including the total ground state, three local excited states in each chromophore, and six charge transfer states from one chromophore to the other, and *vice versa*. The energies of C.T. transitions and the Coulombic repulsions between local transitions were calculated using Ohno approximation.8) The configuration interaction energies between C.T. states, or between C.T. and local excited or ground states were calculated by the use of the value of 0.2 β (-0.48 eV)1)2c) for exchange integrals between orbitals adjacent to the spiro center ($= \beta_{spiro}$). The dipole and rotational strengths of the resulting excited states were given by dipole velocity method in which the contributions of C.T. components were evaluated with the calculated value of ∇_{spiro} (0.567×10^7 cm^{-1}).

The results are given in Figure 2 and Table 2. The dipole and rotational strengths were found to be dominated by local transition components. C.T. components were found to make minor contributions to those strengths because of their small bond moments, but to play a very important part in the determination of transition energies of the composite molecule, viz., spirobiindene.

Table 1. The transition moments and dipole strengths for indene.



exited state	energy eV (nm)	dipole strength ($\times 10^{35}$)	angle between the transition moment and X-axis	component of transition moment ($\times 10^{18}$)	
				X	Y
^1L_a	5.08(244)	1.210	-102.1°	-0.731	-3.401
^1B_b	6.16(201)	0.582	+2.5°	2.411	0.107
^1B_a	6.52(190)	1.016	+68.0°	1.195	2.956

Table 2. The calculated energies and mixing coefficients of the electronic states of spirobiindene.

energy (nm)	N1)	mixed excited state2,3,4)
283	1B	$+0.37\,L_1 + 0.56\,CT_1$
281	1A	$+0.33\,L_1 - 0.57\,CT_1$
236	2B	$+0.55\,L_1 - 0.33\,CT_1$
233	2A	$+0.57\,L_1 + 0.36\,CT_1$
225	3B	$- 0.52\,CT_2$
216	3A	$- 0.66\,CT_2$
215	4B	$- 0.64\,CT_3$
214	4A	$- 0.65\,CT_3$
199	5A	$+0.63\,L_2$
197	5B	$-0.63\,L_2$
194	6B	$-0.54\,L_3 - 0.34\,CT_4$
184	6A	$+0.39\,L_3 - 0.56\,CT_4$
182	7B	$+0.29\,L_3 - 0.58\,CT_4$
179	7A	$-0.54\,L_3 - 0.36\,CT_4$

1) Number and symmetry of the electronic states in C_2 system.

2) Only the main components which contribute to the energies of the transitions are listed.

3) $L_i = \Psi_i^M a \pm \Psi_i^M b$: $\Psi_i^M a$ and $\Psi_i^M b$ represent the locally excited configuration of monomeric indene chromopnore a and b (^1L_a, ^1B_b, and ^1B_a for $i = 1$, 2, and 3, respectively). The plus sign is for A symmetry and minus sign for B symmetry.

4) $CT_i = \varphi_k^a \varphi_l^b \pm \varphi_l^a \varphi_k^b$: $\varphi_k^a \varphi_l^b$ represents the charge transfer state from kth wave function φ_k of indene a to lth wave function φ_l of indene b ; k=4, l=5 for i=1 (4.731 eV), k=4, l=6 for i=2 (5.681 eV), k=3, l=5 for i=3 (5.681 eV), k=3, l=6 for i=4 (6.621 eV), k=4, l=7 for i=5 (6.815 eV), k=2, l=5 for i=6 (6.815 eV). The plus and minus signs have the same meaning as given above.

ca. [illegible] nm.

ca. [illegible] nm.

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