Optically Active Spiro[4.4]nonane Derivatives: Syntheses and Circular Dichroism of Homoconjugated Dienes and Diketimine Derivatives

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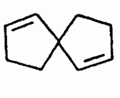
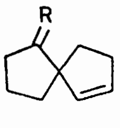
Summary (+)-(5*S*)-Spiro[4.4]nona-1,6-diene (**1**), (+)-(5*S*)-6-methylenespiro[4.4]non-1-ene (**2**), (+)-(5*R*)-1,6-dimethylenespiro[4.4]nonane (**4**), and four diketimine derivatives from (−)-(5*S*)-spiro[4.4]nonane-1,6-dione (**5**) were prepared; their chiroptical behaviour in the $\pi \rightarrow \pi^*$ region was consistent with expectations based on the exciton model, except for (**1**).

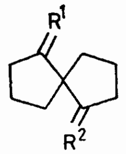
Spiro[4.4]nonane derivatives of C_2 symmetry with dissymmetrically arranged simple chromophores such as (**1**) and (**5**) have been studied in detail by several groups.[1–7] A satisfactory interpretation has been given for the relationship between the observed c.d. and the absolute configuration of (**5**),[4–6] but no unanimous conclusion has been drawn for (**1**)[2b,6,7] even by the SCF–CNDO–CI method.† We have now prepared some spirodienes (**1**),‡ (**2**), and (**4**), which differ from one another in mutual disposition of two double bonds without serious alteration to the carbon skeleton. The diketimine derivatives (**7**)—(**10**), which are similar to the diene (**4**) in the arrangement of chromophores, were also prepared.



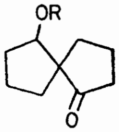
(1)



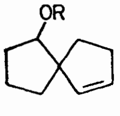
(2) $R=CH_2$
(3) $R=O$



(4) $R^1=R^2=CH_2$
(5) $R^1=R^2=O$
(6) $R^1=O, R^2=CH_2$
(7) $R^1=R^2=N-OH$
(8) $R^1=R^2=N-NHCONH_2$
(9) $R^1=R^2=N-NHC_6H_4NO_2$-*p*
(10) $R^1=R^2=N-NHC_6H_3(NO_2)_2$-*o,p*

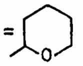


(11)

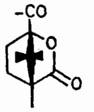


(12) R = H

R =



(13a),(13b) R =



Racemic *cis*-spiro[4.4]non-6-en-1-ol (**12**) was obtained in 19% yield from the tetrahydropyranyl ether (**11**) of racemic *cis*-6-hydroxyspiro[4.4]nonan-1-one by the procedure previously reported.[8] (**12**) was converted into a diastereomeric mixture of camphanates, which was separated by fractional recrystallization successively from n-hexane and methanol to give (−)-(**13a**) {$[\alpha]_D^{20}$ −131·7° (MeOH), m.p. 130·9—131·3 °C} and (+)-(**13b**) {$[\alpha]_D^{20}$ +125·0° (EtOH), m.p. 83·8—85·2 °C}.§ The latter was hydrolysed under alkaline conditions, followed by oxidation with CrO_3–pyridine complex, to yield the known (+)-(5*S*)-spiro[4.4]non-6-en-1-one (**3**) {$[\alpha]_D^{20}$ +310° (iso-octane)}.[8] Wittig reaction (Ph_3PMeBr and Bu^tOK in pentane) of this enone gave (+)-(5*S*)-6-methylenespiro[4.4]non-1-ene (**2**) {$[\alpha]_D^{20}$ +109° (iso-octane), b.p. 70 °C (bath temp.) at 100 mmHg, yield 44%}. An analogous reaction of (+)-(5*R*)-6-methylenespiro[4.4]nonan-1-one (**6**)[8] yielded (+)-(5*R*)-1,6-dimethylenespiro[4.4]nonane (**4**) {$[\alpha]_D^{20}$ +190° (iso-octane), yield 18%}. (+)-(5*S*)-Spiro[4.4]nona-1,6-diene (**1**) {$[\alpha]_D^{20}$ + 119·3° (pentane)}‡ was prepared starting from (5*S*)-spiro-[4.4]nonane-1,6-dione (**5**)[2a] by Cram's procedure.[1b] The diketimine derivatives (**7**)—(**10**) were prepared from the (5*S*)-dione (**5**) in the usual way.

We have applied the exciton theory[9] to these dienes using the point-dipole approximation for the $\pi \rightarrow \pi^*$ transition moment, which we placed at the midpoint of each double bond and directed along the bond axis. The signs of the couplets observed for (**2**) and (**4**) agreed with those expected for all the possible conformations examined with molecular models, though the maximum in the higher frequency region could not be reached (see Table). The diketimine derivatives (**7**)—(**10**) showed couplets in fair agreement with those expected from an analogous application of the theory. However, the sign of the lower frequency region in the c.d. spectra observed for (**1**)‡ was opposite to those predicted for all conformations except for a rather unfavourable one, as already pointed out by Wynberg.[7]

Table

U.v. and c.d. spectra of spirodienes and diketimine derivatives.

		U.v.		C.d.	
Compound	Solvent[a]	λ/nm	ϵ_{max}	λ/nm	$\Delta\epsilon_{max}$
(5*S*)-(**1**)	A	198·5	12,000	197·5	+13·4
				184[c]	(+ 3·3)
(5*S*)-(**2**)	B	186	15,600	199·5	+16·4
				186·5[c]	(− 6·8)
(5*R*)-(**4**)	B	187	13,300	211·5	+29·6
				186·5[c]	(−31·9)
(5*S*)-(**7**)	B	196·5	10·600	215·5	−23·8
				193·5	+26·4
(5*S*)-(**8**)	C	232·5	22,800	240	−52·6
		215sh	16,500	209	+25·8
(5*S*)-(**9**)	C	395	47,500	413·5	−63·2
				366	+32·1
(5*S*)-(**10**)	C	430sh[b]	10,800	432	+63·2
		365	39,200	372	−81·0
				333	+21·6

[a] A: n-hexane, B: iso-octane, C: MeOH. [b] Assigned to $n \rightarrow \pi^*$ transition of the nitro group. [c] Lowest wavelength measured.

† Satisfactory results were reported in refs. 2b and 6b, but calculations with the parameters proposed by Del Bene and Jaffé gave a result in disagreement with that observed. See ref. 7.

‡ In the c.d. spectra of the diene (**1**), we could find no small negative maximum in the longest wavelength region. Such a small negative c.d. (225 nm), as described in ref. 2b, might be attributed to minute quantities of contaminants probably caused by a difference in the synthetic method. Our discussion on the diene (**1**) is based on the assignment of the c.d. maximum at 197·5 nm to the longest wavelength $\pi \rightarrow \pi^*$ transition (B-symmetry), which was also shown by the concordant u.v. maximum (198·5 nm).

§ Satisfactory elemental analyses were obtained for new compounds and their i.r. and n.m.r. spectra are in accord with the assigned structures.

In contrast, when the allylic bond polarization model[10] extended to homoconjugated dienes was employed as an alternative, the expected sign of the lower frequency c.d. band agreed with that observed for (**1**) as well as for (**4**). Also the c.d. of (**2**) was explicable by this model, if the lower frequency band was assigned to the *endo*-olefin.

Thus, in contrast to the case of (**2**) and (**4**), exciton coupling and allylic bond polarization exert opposite effects on the c.d. spectrum of the diene (**1**). The apparently anomalous Cotton effect of (**1**) might be attributed mainly to allylic bond polarization.

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