Optically Active Spiro[4.4]nonane Derivatives: Syntheses and Circular Dichroism of Bis-αβ-unsaturated Ketones

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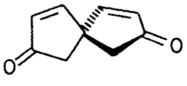
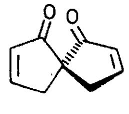
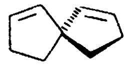
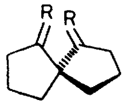
Summary (5*S*)-Spiro[4.4]nona-3,8-diene-2,7-dione (**1**) and (5*S*)-spiro[4.4]nona-2,7-diene-1,6-dione (**2**) have been prepared; the c.d. of (**1**) in the longest wavelength $\pi\rightarrow\pi^*$ region shows the opposite sign to that predicted by exciton theory as in the case of spiro[4.4]nona-1,6-diene (**3**).

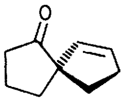
WHILE investigating the optical activity of chiral spiro[4.4]nonane derivatives, we noted that the observed c.d. sign of the diene (**3**) in the longest wavelength $\pi\rightarrow\pi^*$ region was opposite to that expected from exciton theory, in sharp contrast to the dienes (**5**) and (**6**).[1] This apparently anomalous chiroptical behaviour was ascribed to the effect of allylic bond polarization[2] overriding the opposite effect of exciton coupling between the $\pi\rightarrow\pi^*$ transitions of the double bonds. For further clarification of this point, we have prepared the bis-$\alpha\beta$-unsaturated ketones (**1**) and (**2**), in which exciton coupling might possibly become the dominant factor, owing to the red shift of the absorption band. Moreover, since these compounds have relatively rigid structures, analyses of their c.d. spectra should not be complicated by uncertainty in conformation as is the case with (**3**).[1,3]

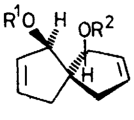

(1)

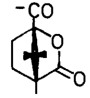

(2)


(3)


(4) R = O
(5) R = CH$_2$


(6)

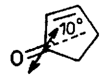

(7) R^1 = R^2 = H
(8) R^1 = H,
R^2 = COC$_6$H$_4$NO$_2$-*p*

(9) R^1 =

R^2 = COC$_6$H$_4$NO$_2$-*p*

The (5*S*)-diene (**3**),[1] prepared from optically pure (5*S*)-(**4**) by Cram's procedure,[4] was brominated using *N*-bromosuccinimide, followed by treatment with Et$_4$NOAc, to afford the diacetate, which, after methanolysis, was oxidized with active MnO$_2$ to give (5*S*)-(+)-(**1**) {[α]$_{\mathrm{D}}^{20}$ +97° (MeOH), m.p. 104·5—107·2 °C, 11% yield from (**3**)}.†

The optically active bis-enone (**2**) was prepared starting with optical resolution of a racemic mixture of the *trans-cis*-diol (**7**), prepared by Semmelhack's procedure,[5] since bromination of (**4**), followed by dehydrobromination, gave (**2**) in very poor yield. Treatment of (**7**) with an equimolar amount of *p*-nitrobenzoyl chloride in benzene–pyridine gave a mixture of two diastereomeric monoesters which was separated by column chromatography on silica gel. The less polar portion (**8**)‡ was treated with (−)-camphanyl chloride in pyridine, and the resulting diastereomeric mixture of camphanates was separated in a similar manner. The more polar portion was recrystallized from cyclohexane to give (+)-(**9**) {[α]$_{\mathrm{D}}^{20}$ +32·5° (benzene), m.p. 136·4—137·4 °C}, which, upon methanolysis, produced the diol (+)-(**7**) {[α]$_{\mathrm{D}}^{20}$ +13·6° (EtOH), m.p. 115·7—116·1 °C, yield 61%}. Oxidation of (+)-(**7**) with Jones' reagent afforded (−)-(**2**) {[α]$_{405}^{20}$ −127° (MeOH), m.p. 60·3—63·0 °C, yield 23%}. Reduction of (−)-(**2**) over Adams catalyst, followed by oxidation with Jones' reagent, gave the known (5*S*)-(−)-(**4**)[6], thus establishing the absolute configuration of (−)-(**2**) as (5*S*).

The chiroptical behaviour of these bis-enones in the $\pi\rightarrow\pi^*$ region (*ca.* 220 nm) was examined on the basis of the exciton model.[7] While the direction of the $\pi\rightarrow\pi^*$ transition moment has already been investigated in detail with cyclohexenones,[8] data are not available for cyclopentenones. Therefore, we estimated its direction from HMO calculations, assuming that the cyclopentenone unit adopts a planar conformation. The transition moment was found to lie at an angle of *ca.* 10° to the carbonyl bond [see (**A**)].



(A)

The calculated splittings for (**1**) and (**2**) were 2960 and 1280 cm^{-1}, respectively, when each point-dipole was placed at the centre of the C$_\alpha$–C$_\beta$ bond. If the point-dipole was located at any point in each enone chromophore or its vicinity, it was calculated that the B-symmetry coupling always appeared at a lower frequency than A, unless the direction of the transition cited above was seriously modified.§

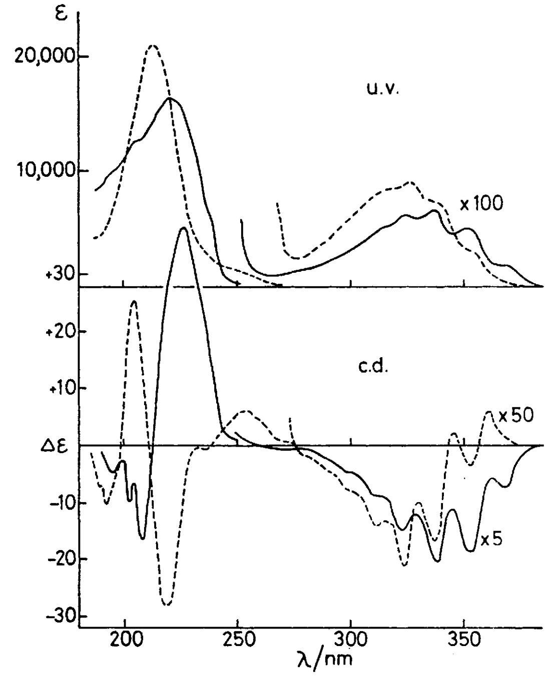


FIGURE. U.v. and c.d. spectra of (5*S*)-(+)-spiro[4.4]nona-3,8-diene-2,7-dione (**1**) (———) and (5*S*)-(−)-spiro[4.4]nona-2,7-diene-1,6-dione (**2**) (– – – – –) in iso-octane.

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† All new compounds gave satisfactory elemental analyses, and i.r. and n.m.r. spectra.

‡ The configuration of the ester group was determined by comparison of its n.m.r. spectra with that of (**7**).

§ The interaction energy was checked by calculating the repulsion between the transition monopoles by the Ohno approximation using the same HMO coefficients (K. Ohno, *Theor. Chim. Acta*, **1964**, **2**, 219.) The computation on B-coupling gave a negative value for (**1**) (−370 cm^{-1}), but a slightly positive one for (**2**) (+70 cm^{-1}) in contrast to the exciton model. However, negative values were found for the latter when the repulsion was calculated with preferred envelope conformers of the C_2 type whose apical carbon atoms are displaced by 0·1 Å or more. Calculation for (**1**) gave negative values with all conformers. The contribution from homoconjugation between enones seemed to stabilize the B-coupling mode in any conformation of both bis-enones.

The c.d. spectrum observed for (5*S*)-(**2**) showed a negative couplet in the $\pi \rightarrow \pi^*$ region in agreement with that expected from the calculated repulsion (see Figure).¶ In contrast to prediction, however, a positive couplet was observed for (5*S*)-(**1**), its lower frequency band being markedly strong.** It is evident that the exciton model, considering the enone π-system alone, could not explain this chiroptical property. Thus, the anomalous c.d. behaviour of the homoconjugated (**3**) has been retained by the bis-enone (**1**), in spite of the red shift of the $\pi \rightarrow \pi^*$ absorption. These facts indicate that the contribution of the allylic bond polarization to the c.d. of (**3**) and its analogues is dominant, as was pointed out in the case of monoenones.[9]

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¶ The origin of the absorption at *ca.* 250 nm which is shown as a minute shoulder in the u.v. spectrum is still unknown.

** The negative c.d. absorption on the higher frequency side seems to be overlapped by the positive absorption of another (possibly $n \rightarrow \sigma^*$) transition.

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