The Circular Dichroism Spectrum of Spirobihydantoin

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SPIROBIHYDANTOIN is a rigid, bicyclic molecule which is optically active but contains no asymmetric carbon atom. Its structure is shown in the Figure, but, its absolute configuration not being established, it is not known if this represents the (+)- or (−)-enantiomer. Its optical properties are of interest because of its fixed conformation and because its chromophoric groups are related to those of polypeptides and nucleotide bases. We have synthesized and resolved it by the method of Pope and Whitworth.[1] The (+)- and (−)-enantiomers showed equal and opposite rotations and c.d. bands; data are shown here only for the (−)-form. The structure was confirmed by elemental analysis and by its n.m.r. spectrum in [$^2H_6$]dimethyl sulphoxide, which showed singlets at τ 1·27 and τ −0·50 for H(1) and H(3), respectively,[2] the former being much narrower, probably as a result of more effective nitrogen quadrupole relaxation.[3] Absorption and c.d. spectra were obtained using a Durrum-Jasco model ORD/UV/5 spectrometer with c.d. modification.

The c.d. spectrum of (−)-spirobihydantoin (Figure) appears to exhibit at least five bands, which we number consecutively from right to left. The oppositely signed bands 1 and 2 are relatively weak and have been magnified 25-fold in the Figure. The marked red-shift of these two bands on going from water to ethanol to tetrahydrofuran suggests their origin to be n–π^* transitions. Bands 3, 4, and 5 show little solvent shift and may be assigned to π–π^* transitions. Bands 4 and 5 resemble those in the spectra of right-handed α-helical polypeptides, and might be similarly attributed to exciton splitting of the π–π^* transition. Support for the exciton interpretation is furnished by the c.d. spectrum of the simple hydantoin obtained from L-leucine and urea which shows two broad bands with negative maxima at 238 mμ ($\Delta\epsilon$ = − 1·6) and at 198 mμ ($\Delta\epsilon$ = − 2·8). The marked difference in the relative intensities of the corresponding bands in spirobihydantoin at 245 mμ ($\Delta\epsilon$ = − 1·9) and at 198 mμ ($\Delta\epsilon$ = − 38) suggest that the enhanced intensity at the shorter wavelength is due to ring-ring interaction. But because of the present state of uncertainty in assignments in this wavelength region in amides and related chromophores,[4] such assignments must be regarded as tentative.

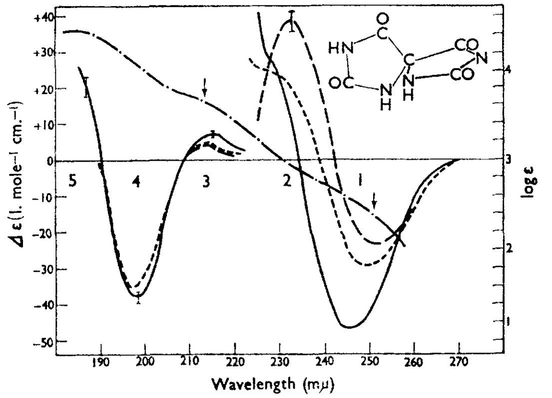

FIGURE. *Circular dichroism and absorption spectra of (−)-spirobihydantoin.*

(——) C.d. spectra in water; (- - -) in ethanol; (— — —) in tetrahydrofuran; (— · —) in water.

For bands 1 and 2 of the c.d. spectra, the scale readings on the left-hand ordinate should be divided by 25. Arrows indicate where pronounced shoulders can be observed in the u.v. spectrum in tetrahydrofuran.

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