

## Thermodynamics of Hydrogen Bond Formation from Temperature Dependent C.D. Spectroscopy

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A linear regression analysis of c.d. data is used to obtain enthalpies and entropies of formation of cyclic hydrogen-bonded dimers of all-*trans*-retinal and hexadienal Schiff bases.

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We have shown recently<sup>1</sup> that the Schiff base (**1**) obtained from all-*trans*-retinal aggregates in aprotic solvents to form what we assume is a hydrogen-bonded cyclic dimer ( $A_2$ ). Starting with a chiral amine, the formation of the homochiral dimer is shown by c.d. spectroscopy; with the polyene chains extending from the same face of the ring, interaction of the chromophores results in two excitations separated by twice the

interaction energy and each associated with high rotatory strength of opposite sign. Analysis of u.v. and c.d. intensities led us to propose a structural model in which the two chromophores make an acute angle of about 60° with each other.

The aggregation is strongly temperature and concentration dependent. In Figure 1, the symbols denote the combined  $\Delta\epsilon$



Hydrogen bonded complexes of retinal Schiff bases have recently become a focus of attention concerning the photochemistry of these biologically important systems.<sup>7</sup> With respect to the proton translocation postulated<sup>8</sup> on the basis of i.r. evidence for the hydrogen bond formed between all-*trans*-retinal Schiff bases and phenol,  $-O-H \cdots N= \rightleftharpoons -O^- \cdots H-N^+=$ , we have found that in very dilute solutions at low temperatures the observed split Cotton effects we observe in our dimers coalesce giving way to long-wavelength absorptions. Whether these are due to (protic) impurities in the solution or present genuine proton translocations in the dimer is the subject of ongoing investigation.

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