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THE NATURE OF THE EXCITED STATES IN ALL-TRANS-RETINAL SCHIFF BASES

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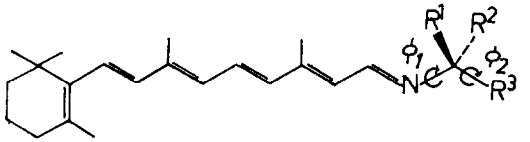
Summary: The temperature dependent CD spectra of two chiral Schiff bases of all-*trans*-retinal reveal a three-band absorption pattern for the retinal chromophor. A preliminary analysis suggests that the band at 260 nm corresponds to the *cis*-peak.

Despite the continuing interest the retinal isomers command both from experimental and theoretical viewpoints[1] many basic questions regarding their electronic structure and the stabilities of excited states remain unanswered. Thus, while it is generally agreed that the high intensity absorption of these compounds at ~365 nm (~350 in the Schiff bases) corresponds to the $^1B_u^+$ state (symbols according to C_{2h}-symmetry of the chromophor) the wave length of the $^1A_g^+$ state is not clear at all. This *cis*-peak has been variously assigned to the γ-band at ~250 nm[2] or to the β-band at 280 nm [3,4] the ambiguity arising from the low intensity of this absorption band, even in the various *cis*-isomers, next to the very intense $^1B_u^+$ transition.

We have determined the temperature dependent CD spectra of the Schiff bases of all-*trans*-retinal with both the (*R*)- and (*S*)-enantiomers of 1-phenylethylamine, **1** and **1a**, and 1-(1-naphthyl) ethylamine, **2** and **2a**, and present what can be inferred from the spectra and theoretical calculations about the assignment of the different absorption bands. The room temperature CD spectrum of **2a** has been used before by others[5] who showed that the CD bands could be interpreted as arising from the interaction between the long wave length transition of the planar polyene chromophor with the aromatic transitions. No assignment of higher energy states was attempted, however, since the corresponding absorptions of the retinal chromophor were not entered into the calculations.



	R^1	R^2	R^3
1	H	CH_3	phenyl
1a	CH_3	H	phenyl
2	H	CH_3	1-naphthyl
2a	CH_3	H	1-naphthyl

The UV and CD spectra of **1** and **2** in *i*-pentane are shown in the Figure[6]. The CD spectrum of **1** consists of a three-band pattern with alternating signs and maxima occurring at 370, 260 and 220 nm which originate in the retinal system. The phenyl absorptions are expected at about 260 nm (α-band) and 200 nm (p-band); the former is calculated to have very little rotational strength, while the latter is probably outside the spectral range probed.

The CD spectra of **2** are more complex since the aromatic transitions are shifted bathochromically and become clearly discernible. Again we ascribe the bands at 360, 250 and 225 nm to the retinal absorptions, their signs being the same as in 1 which has the same absolute configuration. The other bands are aromatic in nature: the α-band reveals itself as a positive bump at 313 nm (calculated with low rotational strength at 315 nm); the p-band has a well-resolved vibrational fine structure with maxima at 295, 285 and 275 nm (values identical in the UV), while the β-band rises, in the low-temperature-spectra, as a positive sharp peak out of the broad third negatively signed retinal absorption.

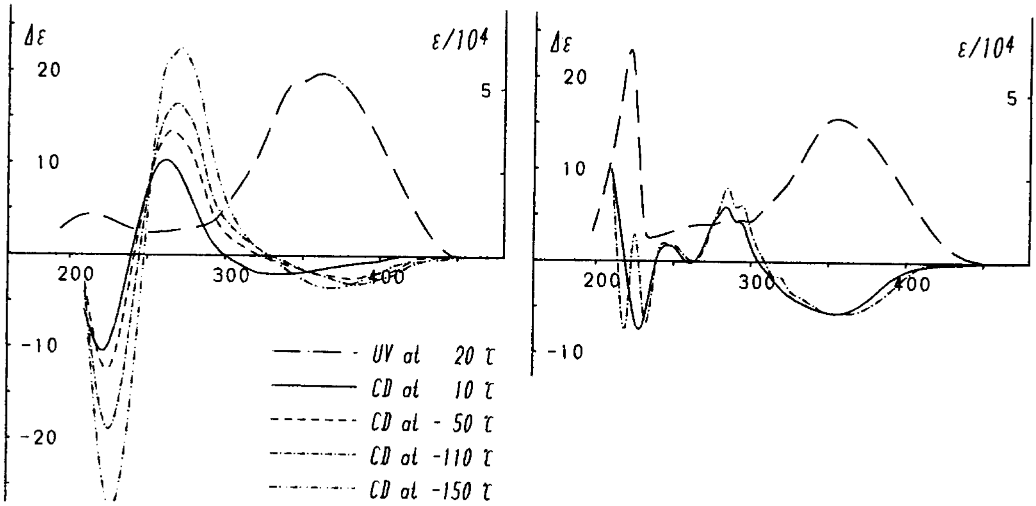


Figure: UV and temperature dependent CD spectra of 1 (left) and 2 (right) in *i*-pentane.

Our assignment is supported by the CD spectra of Schiff bases obtained by condensing all-*trans*-retinal with aliphatic chiral amines, such as 2-aminopentane, $H_2N\text{-}CH(CH_3)C_3H_7$, or 2-aminobutane, $H_2N\text{-}CH(CH_3)C_2H_5$.[7] These compounds show CD absorptions, with rotational strengths about an order of magnitude smaller than 1 and 2, with the same alternating sign pattern and maxima at 360, 255 and 220 nm. Lacking a chromophor in the amine part, these absorptions have to originate in the retinal π-system the transitions being asymmetrically perturbed by the chiral substitution.

The temperature dependence of the CD absorptions is much more pronounced in 1 than in 2 indicating a higher degree of conformational lability of the phenyl compound than the naphthyl analogue. We have used the Moscowitz-Djerassi treatment[8] to analyze the behaviour of 1 and found that the data do not fit an equilibrium between two chiral species if rigid criteria are applied. The reason is probably that the equilibrium involves more than two conformations. For a two-component equilibrium the data which fit the experiment best[9] are given in Table 1. They correspond to species with close to mirror-like CD absorptions.

For a preliminary interpretation of the spectra calculations were performed based on a coupled oscillator model[10] with the following assumptions: (1) all double bonds of the all-*trans*-retinal chromophor (locked into a planar s-*cis*-configuration about the C(6)-C(7)-bond) were represented by identical oscillators (λ_0 = 157 nm) their interaction being calculated by the extended dipol model[11] and scaled to correctly reproduce the 364 nm absorption of a conjugated polyene with six double bonds[12]; (2) aromatic transitions were represented by oscillators of lengths and frequencies corresponding to experimental oscillator strength and energies.

Table 1: Experimental[a] and calculated[b] rotational strengths (in 10^{-40}cgs) of 1

wave length	370 nm	262 nm	260 nm	220 nm	200 nm
more stable isomer[a]	-18	-	110	-110	-
less stable isomer[a]	9	-	-130	145	-
H-eclipsed	-16 ... 16	-1.6 ... 1.6	160 ... 200	-	-120
CH_3-eclipsed	-8 ... -8	-1.6 ... 1.6	-160 ... -180	-	180
phenyl-eclipsed	-2 ... 2	-2.5 ... 2.5	-20 ... 20	-	0
assignment	$^1B_u^+$,retinal	α, phenyl	$^1A_g^+$,retinal	retinal	p,phenyl

a) from regression analysis assuming an equilibrium between two isomers; b) range of values according to range of ϕ_2 (0 ... 360°)

Table 2: Experimental[a] and calculated rotational strengths (in 10^{-40}cgs) of 2

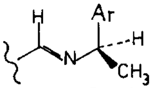
wave length	360	313	285	250	225[b)]	225[c)]
experimental	-34	> 0	27	+5	-15	+9
H-eclipsed,ϕ_2=-50°	-46	0,8	104	-159	-	30
H-eclipsed,ϕ_2=150°	-31	0,1	156	-171	-	5
assignment	$^1B_u^+$,retinal	α,naphthyl	p,naphthyl	$^1A_g^+$,retinal	retinal	β,naphthyl

a) from spectrum at room temperature; b) broad signal; c) very sharp signal

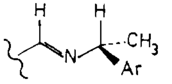
The relative orientation of the polyene and the aromatic chromophor is completely described by the dihedral angles ϕ_1 and ϕ_2 which characterize, respectively, the conformation at the chiral carbon atom with respect to the plane of the polyene and the rotation of the aromatic system along its attachment bond. Varying the two angles in 15° increments the rotational strengths of the different excitations in all possible conformations were calculated for 1 and 2. From these data a possible picture emerges about the azomethine conformations and the probable band assignments.

Of the three conformations which leave the azomethin double bond eclipsed with respect to the three carbon substituents the aryl eclipsed form appears from models to be the most hindered.

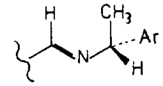
aryl-eclipsed:



hydrogen-eclipsed:



methyl-eclipsed:



For 1 we base our analysis primarily on the 260 nm band the CD of which is calculated to be almost independent of ϕ_2. This is important since rotation of the phenyl group is certainly very easy.[13] For the hydrogen-eclipsed form we calculate a positive, for the methyl-eclipsed one a negative CD. Considering the increase of the rotational strength at low temperatures this indicates that the former is the more stable conformation. It is tempting to correlate the strong negative band at 220 nm with the calculated p-band values; however, the evidence including the data from 2 indicate that this transition involves either the forbidden $^1A_g^-$ or a higher $^1B_u^+$ absorption both of which are outside the scope of our model. The 370 nm rotational strength is, like the one of the 262 nm transition, highly dependent on ϕ_2, so we would not attempt to base our analysis on this absorption. We note, however, that the magnitudes of the calculated values are within the experimental range.

The spectrum of 2 is less temperature dependent which indicates an increased preference for one conformation already at room temperature. This is understandable considering that the naphthyl group is spacially more demanding than the phenyl group. Again we begin our analysis with the p-band at 285 nm and its constant positive rotational strength. The calculated value of this absorption changes sign only when the naphthyl group moves from one side of the retinal plane to the other; it is almost independent of ϕ_2. This rules out any significant participation of methyl-eclipsed like conformations which leave the naphthyl group on the "wrong" side of the molecule.

In contrast to the rather robust behaviour of this band the rotational strengths of all other absorptions show a complicated dependence on ϕ_1 and ϕ_2 including several changes of sign. There is in particular not one conformation for which the 250 and the 225 nm band are equally signed as is found experimentally. For two conformations which from molecular models appear feasible the calculated rotational strengths are given in Table 2. In one (ϕ_2= -50^{0}) the C(8)-hydrogen of the naphthyl ring is staggered between the hydrogen and the methyl group, in the other (ϕ_2= 150^{0}) it lies between the methyl group and the nitrogen free electron pair. Except for the 250 nm band the rotational strengths of all absorptions are correctly reproduced in sign and magnitude.

We think there is conclusive evidence for the assignment of the three naphthalene bands. This leaves for the 250 nm absorption only the $^{1}A_g^{+}$-assignment, in agreement with 1 and with the finding of Becker *et.al.*[14] Considering the disagreement between calculated and observed rotational strengths especially for this band, however, more sophisticated calculations are needed, which hopefully will reveal also the nature of the 225 nm band.[15]

Acknowledgement: Dr. Kolster provided the computer program for the regression analysis.

References and Notes:

(1) For recent reviews see (a) Ebrey, T.; Honig, B. Q.Rev.Biophys. 1975, 8, 125; (b) Honig, B. Ann.Rev.Phys.Chem. 1978, 29, 31; (c) Birge, R.R. Ann.Rev.Biophys.Bioeng. 1981, 10, 315

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(5) Johnston, E.M.; Zand, R. Biochem.Biophys.Res.Comm. 1972, 47, 712.

(6) Since 1 and 1a show close to mirror-like CD spectra, as do 2 and 2a, we present in the Figure only the spectra of the R-isomers, 1 and 2. All CD spectra are corrected for volume contraction.

(7) Kolster, K. Dissertation Duisburg 1980.

(8) Moscowitz A.; Wellman, K.; Djerassi, C. J.Am.Chem.Soc. 1963, 85, 3515.

(9) The regression analysis for the 370, 260 and 220 nm bands in i-pentane yielded values for ΔG^{0} (in parentheses the linearity coefficients) of, respectively, 1.5 (0.96), 1.7 (0.98) and 1.5 kJ/mol (0.96).

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(11) Nolte, H.J.; Buss, V. Chem.Phys.Lett. 1973, 19, 395.

(12) Karrer, P.; Eugster, C.H. Helv.Chim.Acta 1951, 34, 1805.

(13) The low temperature ^{1}H-nmr-spectrum revealed no temperature dependent signals in the phenyl region down to -80^{0} C.

(14) Schaffer, A.M.; Waddell, W.H.; Becker, R.S. J.Am.Chem.Soc. 1973, 96, 2063.

(15) A referee has questioned our use of a planar retinal chromophor in the calculations since according to crystal structure investigations the cyclohexene double bond is twisted with respect to the rest of the polyene chromophore. This twist almost certainly persists in solution; however, we have not been able to detect this twist in chiral all-trans-retinal Schiff bases. Only when the polyene is shortened to a diene, as in β-cyclocitral Schiff bases, is the interaction between the cyclohexene group and the chiral azomethin group sufficient to allow the CD-spectroscopic detection of this temperature-dependent phenomenon (V. Buss, K. Kolster, U. Wingen, L. Simon, J. Amer. Chem. Soc., in press). For the calculations, we have initially compared the results of a cis-planar conformation with the mean of two oppositely twisted conformations and found the results sufficiently similar to allow the deductions to be made from the planar retinal chromophor.

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