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ELECTRONIC SPECTRA OF 12-*S*-*CIS* CONFORMATIONALLY LOCKED RETINALS

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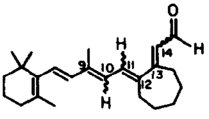
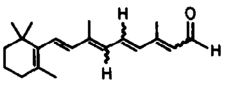
Summary: The electronic absorption spectra of the four new 12-*s*-*cis*-locked retinals (**1a-1d**) bearing 7-*trans*,11-*trans* double bond geometries are described and compared with those of analogous 7-*trans*,11-*cis*-geometries (**1e-1h**) and parent retinals (**2a-h**).

The primary events in the visual[1] and energy transducing[2] processes mediated by rhodopsin and bacteriorhodopsin involve, respectively, photo-induced 11-*cis* → 11-*trans* and 13-*trans* → 13-*cis* isomerizations of the corresponding retinal chromophores.[3] Though much effort has been directed towards an understanding of the photochemistry and electronic absorption spectra of retinoids, there remain many questions regarding the origins of the various bands in these spectra. In this Letter, we report the absorption spectra of the four new 12-*s*-*cis*-locked 7-*trans*,11-*trans*-retinals **1a-1d**,[4] discuss their unusual solvent dependent electronic spectral properties and compare the results to the corresponding data for the 11-*cis*-isomers **1e-h** previously reported[5] as well as parent retinals **2a-h**.



1



2

(E = *trans*; Z = *cis*)

a, $\Delta^9=\Delta^{11}=\Delta^{13}=E$
b, $\Delta^9=Z$; $\Delta^{11}=\Delta^{13}=E$
c, $\Delta^{13}=Z$; $\Delta^9=\Delta^{11}=E$
d, $\Delta^9=\Delta^{13}=Z$; $\Delta^{11}=E$
e, $\Delta^{11}=Z$; $\Delta^9=\Delta^{13}=E$
f, $\Delta^9=\Delta^{11}=Z$; $\Delta^{13}=E$
g, $\Delta^{11}=\Delta^{13}=Z$; $\Delta^9=E$
h, $\Delta^9=\Delta^{11}=\Delta^{13}=Z$

The absorption spectra of retinals generally exhibit a strong α-band absorption at ~360 nm and weaker β- and γ-band absorptions at ~280 nm and ~250 nm, respectively.[3] The α-band is due primarily to a "$^1B_u^{*+}$" state although a "$^1A_g^{*-}$" state is believed to contribute significantly.[6,7] The β-band has been variously assigned to the "$^1B_u^{*+}$" state of 6-*s*-*trans* conformers (present in equilibrium with 6-*s*-*cis* conformers)[8] and to the "$^1A_g^{*+}$" state.[9] The β-[9] or γ-band[8,10] has been identified as the "*cis*" band (so-called because of its prominence in polyenes with *cis* double bonds).[11]

The absorption spectra of the 12-*s*-*cis*-locked 11-*cis*-retinals, **1e-h**, (Fig. 1) support the assignment of the β-band to the "$^1A_g^{*+}$" state (*cis* band) since, in accord with calculations,[9,12] they exhibit very prominent β-bands and weak α-bands. Since these retinals possess no structural feature which would enhance the population of the 6-*s*-*trans* conformers, the proposal that the β-band is 6-*s*-*trans*-conformeric in origin is invalidated. A difficulty with the identification of the β-band as the *cis* band, namely its low energy position, was explained on the basis that the β-band derived most of its intensity from planar 6-*s*-*cis* conformers.[9] The even further red shifted position (295-300 nm) of the β-band in **1e-h** can be explained if the β-band derives greatest intensity from conformations which are both planar 6- and 12-*s*-*cis*, thereby maximizing a double *s*-*cis* induced red shift. Calculations predict the

"$^1A_g{}^{*+}$" state to have greatest oscillator strength in the planar 12-*s*-*cis* conformation.[12] The unusual temperature dependent behavior of 11-*cis*-retinal (increased α- and lowered β- and γ-band intensity[13] and increased quantum efficiency for photoisomerization[14] at low temperatures) has been explained by an equilibrium between 12-*s*-*cis* and 12-*s*-*trans* conformers with preferential stabilization of the latter at low temperatures.[12,10a] The spectra of **2e** (strong β- and γ-bands, moderate α-band) and of the corresponding 12-*s*-*trans* locked analogue (strong α-band, moderate β- and γ-bands) synthesized by Nakanishi[15] provide indirect support for this explanation. The parent 9-*cis*,11-*cis*,13-*cis*- and 11-*cis*,13-*cis*-retinals exhibit spectra very similar (prominent β- and weak α-bands) to that of the corresponding 12-*s*-*cis* locked analogues, **1h** and **1g**, suggesting that these parent retinals exist predominantly as twisted 12-*s*-*cis* conformers.[16]

While prominent β-bands dominate the topology in the spectra of the 11-*cis*-retinals, removal of the 11-*cis* geometry causes increased α-band intensity resulting in a progressive red shift of the low-energy maximum (Fig. 2). Loss of *cis* geometry, particularly at the internal 9- and 11-positions, results in decreased intensity of the β-band in keeping with its assignment as the *cis* band. However, identification of the β-band with the first "$^1A_g{}^{*+}$" state leaves the γ-band unassigned. A noteworthy feature of the spectra of the 12-*s*-*cis* locked retinals is the presence of prominent γ-bands. In fact, the maxima in the 9-*cis*,13-*cis*- and 9-*cis*-retinals, **1d** and **1b**, occur at 251 nm and 255 nm, respectively. Just as in the case of the β-band, successive loss of *cis* geometry results in a progressive decrease of γ-band intensity. These features might suggest that the γ band is associated with a second "$^1A_g{}^{*+}$" *cis*-band. However, PPP-CISD[6,9,12] and INDO-PSDCI[7] calculations do not predict the existence of a second "$^1A_g{}^{*+}$" state in the manifold of valence states with wavelengths above 200 nm. Unfortunately, these same calculations do not provide a convincing alternative assignment for the γ-band (see, for example, Ref. 9). One way to theoretically accommodate a γ band is to distort the 12-13 single bond to near orthogonality to produce a C_5-C_{12} "fragment chromophore". It is important to note, however, that the above situation then removes lower lying transitions from the manifold of calculated states. Thus, the above scenario requires that a small proportion of distorted chromophores generate the γ band while the remaining population with more planar 12-*s*-*cis*-conformations contribute the α and β bands. We believe this hypothesis may have merit and deserves further study.

The 12-*s*-*cis* locked retinals exhibit a red shift of the α-band in polar solvents ($\lambda_{max}^{EtOH} - \lambda_{max}^{hexanes} = 20$ nm for **1a**) of greater magnitude than that observed for parent retinals. There are two possible explanations for this observation. If the change in dipole moment upon excitation is greater in 12-*s*-*cis* versus 12-*s*-*trans* conformers, the enhanced bathochromic solvent shift could be due entirely to this effect. Alternatively, the solvent shift could be due to enhancement of more planar 12-*s*-*cis* conformers in polar solvents due to stabilization of conformers with higher dipole moments. It is likely that both mechanisms contribute for many of the isomers studied here. The absorption spectrum of **1c** exhibits an unusual solvent dependence (Fig. 1). In hexanes, the spectrum has a maximum at 334 nm and a β-band is not defined. However, in ethanol, maxima are observed at 376 nm and 325 nm. The resolution of the 374-nm band is explicable on the basis of a red shift of the "ionic" "$^1B_u{}^{*+}$" state. The

FIGURE 1

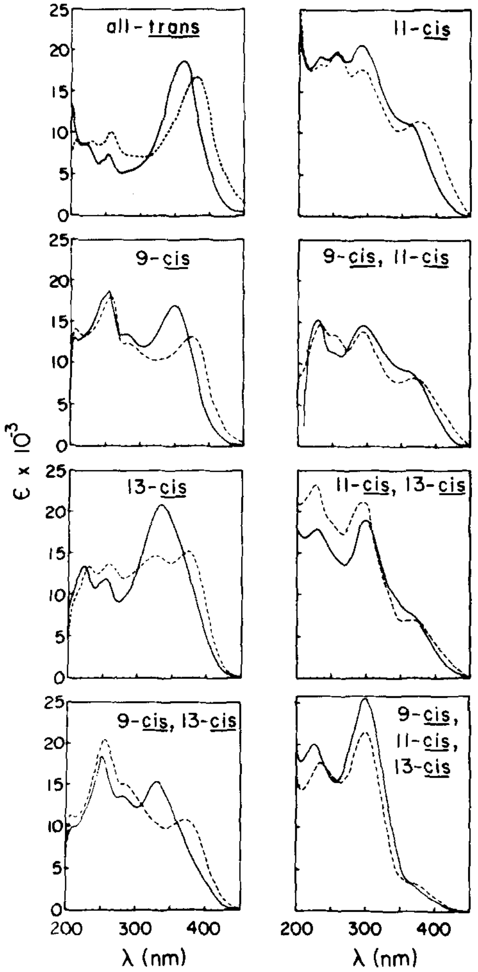


FIGURE 2

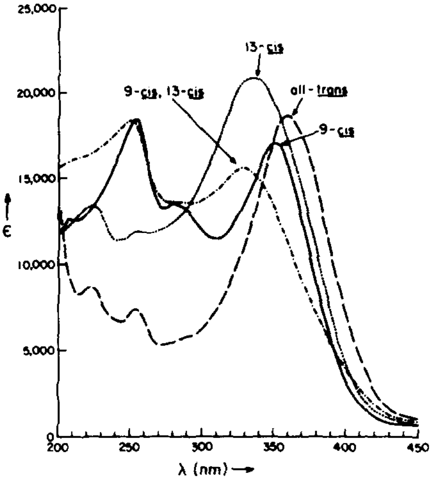
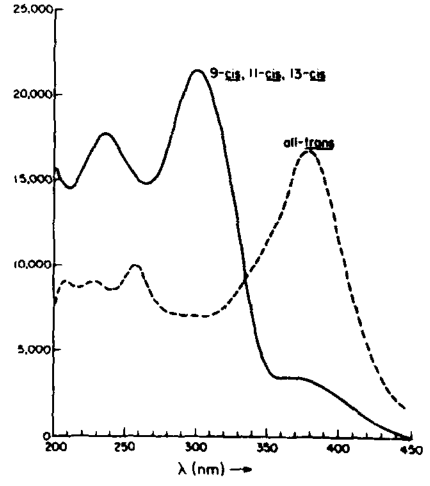


FIGURE 3



Figures 1-3. Absorption spectra of the 12-*s*-*cis*-locked retinals: (1) in hexanes (——) and 95% ethanol (---); (2) the four 11-*trans* retinals **1a-1d** in hexanes; (3) **1a** and **1h** in 95% ethanol.

assignment of the 325-nm band to the "$^1A_g^{*+}$" state, however, poses considerable difficulty since this would invoke an unrealistic red shift for this state. In fact, β-bands are clearly defined at ~290 nm and ~280 nm for **1e** and **1b**, respectively. An interesting possibility is that the 325-nm band is formed by a superposition of "$^1B_u^{*+}$", "$^1A_g^{*-}$" and "$^1A_g^{*+}$" states. Two-photon studies are underway to test this hypothesis. A similar situation obtains for **1d** where the maximum shifts from 329 nm (hexanes) to 372 nm (ethanol). However, for **1d** β-bands are observable at ~280 nm in both solvents and a slight shoulder is apparent at ~325 nm.

The effect of cis linkages on the absorption spectra of retinals is dramatized in this series of compounds as illustrated particularly for **1a** and **1h** (Fig. 3). Much information, useful in the assignment of the various bands in the absorption spectra of retinals, can be derived from these retinals. Further studies are in progress to more fully test the assignments proposed in this Letter.

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