ELECTRONIC STRUCTURE OF POLYENES RELATED TO THE VISUAL CHROMOPHORE

A SIMPLE MODEL FOR THE OBSERVED BAND SHAPES

RUSSELL HEMLEY AND BRYAN E. KOHLER, *Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457, U.S.A.*

ABSTRACT A model is presented which attributes the widths of absorption bands in carotenoids to conformational disorder induced by the β-ionylidene moiety. With reasonable parameter choices, the model gives a good quantitative fit to the spectra observed for four carotenoids and at the same time accounts for the lack of structure in the long-wavelength absorption of retinal.

INTRODUCTION

A striking feature of the optical absorption spectra of retinal and its derivatives, including rhodopsin, is the lack of any resolved vibrational structure, even at liquid helium temperatures. While this spectral diffuseness is very important for the biological function of the visual pigments, it seriously impairs our ability to draw reliable conclusions about the microscopic details of the vertebrate bleaching cycle from the absorption spectra of the various intermediates. In order to develop strategies for obtaining high information content spectra for these systems, it is important to understand the origin of the observed broadening. Some time ago, we examined a series of compounds in which the structural features of retinal were systematically varied (Christensen and Kohler, 1973). These studies demonstrated that the broadening did not correlate with either molecular size or the presence of nonbonded electrons but rather could be associated with the presence of the β-ionylidene ring. From these observations, we concluded that the broadening was a consequence of the presence in the sample ensemble of a large number of conformers differing in the torsional angle about the ring-side chain single bond.

The argument for why the β-ionylidene moiety would give rise to such a broad distribution of conformations is straightforward. One expects strong nonbonded repulsions between the methyl groups on the β-ionylidene ring and the protons on adjacent carbons on the side chain. Those repulsions would raise the energy of the planar conformations which, in the absence of these effects, would represent a significant energy minimum. The raising of this minimum by the nonbonded replusions flattens the dependence of energy on torsional angle, as is nicely demonstrated in some recent calculations (Warshel and Karplus, 1974). At room temperature a wide range of conformations are populated which are frozen in as the temperature is lowered. While the ground-state energy does not significantly depend on this torsional angle, the excitation energy may be expected to vary more strongly. Thus, the absorptions of the various conformers are all shifted with respect to one another with the consequence that when they are superposed the spectrum is completely filled in.

Here we give this model an explicit mathematical form and demonstrate its reasonableness by quantitatively accounting for the observed bandwidths in a series of four carotenoids. The very good fit between the model and the observed spectra encourages the speculation that, in rhodopsin, retinal is indeed present as a large number of conformers.

THE MODEL

Our model for the observed absorption bandwidths in carotenoids is generated in two extremely simple steps. First, we assume that twisting about the ring-side chain single bond can be reasonably viewed as reducing the effective number of double bonds in the molecule n by an amount δn. Each β-ionylidene moiety in the molecule is expected to contribute the same δn: two rings give $2\delta n$.[1] Second, the experimentally determined dependence of the transition energy of the low-energy strong absorption ($^1B_u \leftarrow {}^1A_g$, ground state to the second excited singlet state) on the number of double bonds is used to convert δn into $\delta \bar{\nu}$, the contribution to the absorption bandwidth coming from the distribution of ring-side chain torsional angles.

Fig. 1 shows the dependence of the transition energy on the number of double bonds in conjugation for the first strong absorption for linear polyenes as determined by Sondheimer et al. (1961). The experimental points are fit well by the function

$$\bar{\nu} = 16{,}500 + 64{,}100/n.$$

A spread of δn in the number of bonds in conjugation should make a contribution to the width $|\bar{\nu}| = 64{,}100/n^2\,\delta n$. The actual width will also include contributions from the spread in solvent environments and initial states for the molecules in the ensemble. This, we propose, is roughly constant for a series of polyenes in a given solvent so that

---

[1] For two uncorrelated contributions one would normally write $\sqrt{2}N$. This is appropriate if the deviations from the mean value can have either sign. However, if the most probable configuration is close to the planar one, twisting either way gives shift in the spectrum of the same sign. In this case, even if uncorrelated, the contributions of the two rings add exactly. Given the smallness of the determined δn, we feel that the real distribution of excitation energies is sufficiently skewed that straight addition is appropriate. Using $\sqrt{2}$ rather than 2 increases the standard deviation of fit by a factor of 2. However, given the simplicity of the present model and the relatively small numbers of data, it would not be wise to try to draw deep conclusions about subtle details of the ring-side chain angle distributions at this point.

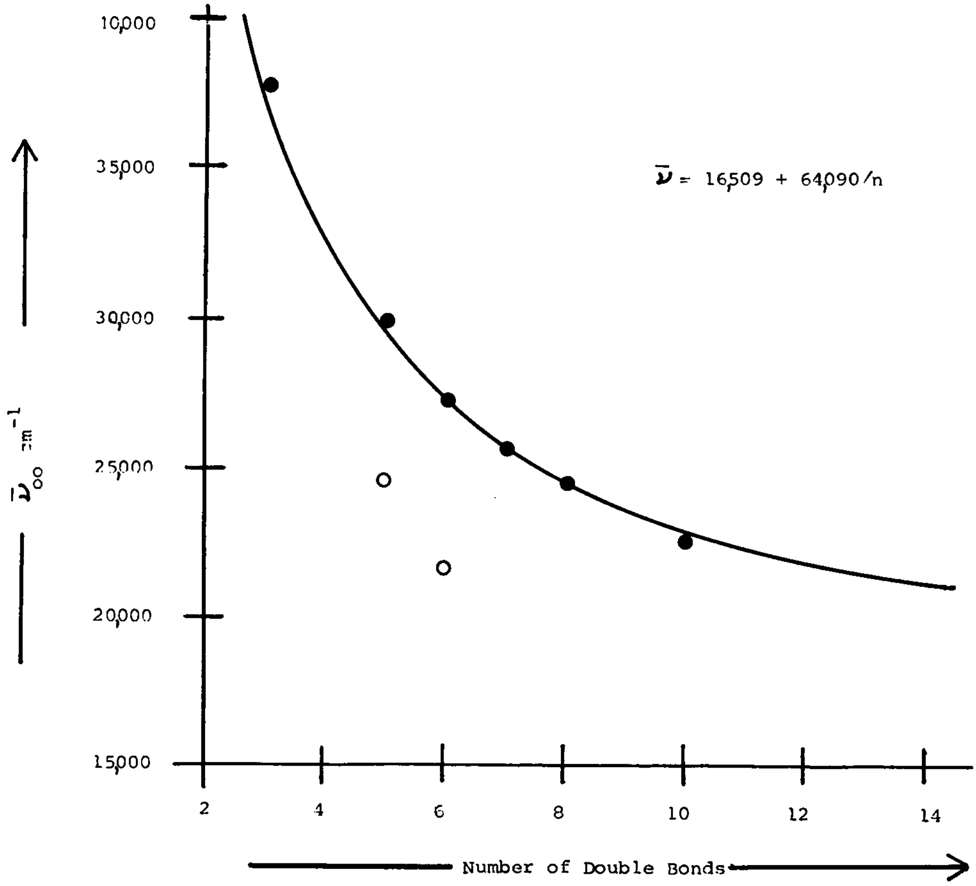

FIGURE 1 Excitation energy as a function of the number of double bonds in conjugation for linear polyenes. The closed circles represent data on the $^1B_u \leftarrow {}^1A_g$ transition as measured by Sondheimer et al. (1961). The open circles are for the $^1A_g \leftarrow {}^1A_g$ transition as measured in high-resolution experiments (Christensen and Kohler, 1975; Christensen and Kohler, 1976). The solid line is the function $\bar{\nu} = 16{,}509 + 64{,}090/n$.

the total width is given by

$$|\delta\bar{\nu}| = \Delta + 64{,}100/n^2\, N\delta n. \tag{2}$$

Δ is the sum of all contributions to the width from factors other than the distribution of torsional angles: N is the number of β-ionylidene rings in the carotenoid (0, 1, or 2) and the rest of the second term gives the width contribution per β-ionylidene ring, given that a ring produces a spread in effective conjugation of δn. Note that there are only two adjustable parameters in this expression, Δ and δn. As a check on the viability of this model, we have looked at the room temperature absorption spectra of four carotenoids where both the number of double bonds, n, and the number of β-ionylidene moieties, N, are varied. These are lycopene, γ-carotene, β-carotene, and decapreno-β-carotene. Their spectra, as previously reported by Vetter et al. (1972), are

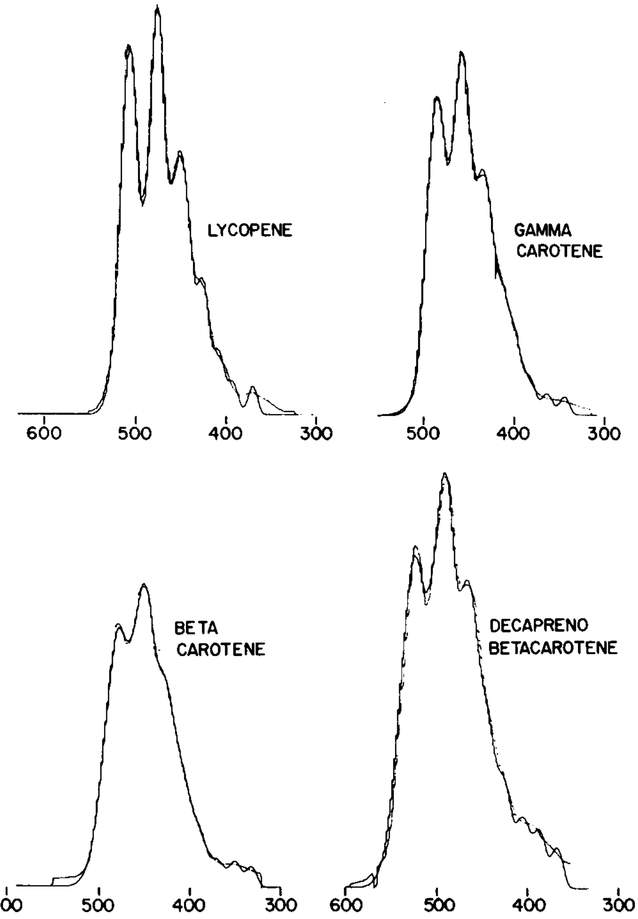

FIGURE 2 Room temperature absorption spectra of lycopene, γ-carotene, β-carotene, and decapreno-β-carotene in hexane as measured by Vetter et al. (1972). The measured spectra and the sum of Gaussians that best fit the measured spectra are superposed.

shown in Fig. 2. To derive an unambiguous measure of width, each spectrum was fit by a superposition of seven gaussians of equal width by least-squares adjustment of the width, positions, and heights of the gaussian functions. For the width $|\Delta\bar{\nu}|$ we have taken the full width at half maximum of the gaussians that gave best fit for each spectrum. In all cases, the lowest energy feature in the spectrum (the zero-zero) was found to contain a single gaussian. The widths measured in this way were then fit by the function $|\delta\nu| = \Delta + 64{,}100/n^2 N\delta n$ by least-squares adjustment of Δ and δn. The results are summarized in Table I. The fit is well within the probable error of experimentally determining the bandwidths and, given the extremely simple form of the model, must be counted as quite successful. The parameter values are quite reasonable. The constant width of 549 cm^{-1} is comparable to kT at room temperature as would be expected, and the spread in conjugation of one quarter of a double bond per

TABLE I

SUMMARY OF WIDTHS OF ROOM TEMPERATURE ABSORPTION SPECTRA OF FOUR CAROTENOIDS

Compound	Number of double bonds	Number of β-ionylidene rings	Measured bandwidth	Calculated bandwidth
	n	N	$\lvert\Delta\bar{\nu}\rvert$	$\Delta + 64{,}100/n^2 N\,\delta n$
Lycopene	11	0	559	549
γ-Carotene	11	1	660	678
β-Carotene	11	2	817	808
Decapreno-β-carotene	15	2	687	688

The best fit parameters are: $\Delta = 549\ \text{cm}^{-1} \pm 14\ \text{cm}^{-1}$,
$\delta n = 0.244 \pm 0.021$.

β-ionylidene moiety is similarly quite reasonable. Some of the approximations made in deriving the bandwidth expression could be improved but, until more extensive data are in hand, this hardly seems worthwhile.

It is of some interest to use this model as parameterized on the longer polyenes to predict absorption bandshapes for the shorter ones, including retinal. To do this, we have taken the spectrum of lycopene to set relative intensities and intervals for the vibronic components. The position of the zero-zero is set by the excitation energy formula (1), and the bandwidths are derived from formula (2) by using the parameters given in Table I. The results for 1-β-ionylidene ring for n = 11, 9, 7, and 5 are shown in Fig. 3. As can be seen, the model that assigns the spectral diffuseness to conformational disorder primarily involving the ring-side chain torsional angle is nicely

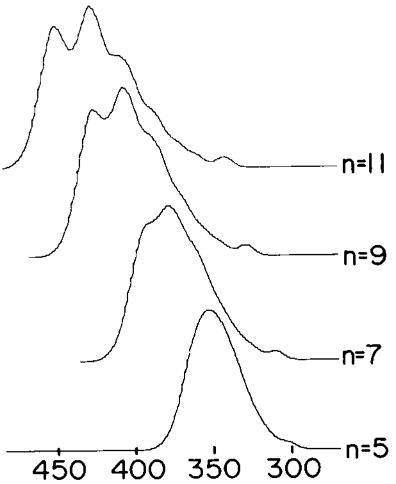

FIGURE 3 Room temperature absorption spectra for a series of carotenoids containing one β-ionylidene ring and n double bonds as calculated from the model.

consistent with both the lack of vibrational structure in retinal and the structured spectra of the longer carotenoids.

Received for publication 1 July 1977.

REFERENCES

CHRISTENSEN, R. L., and B. E. Kohler. 1973. Low resolution optical spectroscopy of retinyl polyenes: low lying electronic levels and spectral broadness. *Photochem. Photobiol.* **18**:293.

CHRISTENSEN, R. L., and B. E. KOHLER. 1975. Vibronic coupling in polyenes: high resolution optical spectroscopy of 2,10-dimethylundecapentaene. *J. Chem. Phys.* **63**:1837.

CHRISTENSEN, R. L., and B. E. KOHLER. 1976. High-resolution optical spectroscopy of polyenes related to the visual chromophore. *J. Phys. Chem.* **80**:2197.

SONDHEIMER, F., D. A. BEN-EPHRIAM, and R. WOLORSKY. 1961. Unsaturated macroscyclic compounds SVII. The prototropic rearrangement of linear 1,5-enynes to conjugated polyenes. The synthesis of a series of vinylogs of butadiene. *J. Am. Chem. Soc.* **83**:1675.

VETTER, W., G. ENGLERT, N. RIGASSI, and U. SCHWIETER. 1972. Spectroscopic Methods. Chapter IV. The carotenoids. O. Isler, editor. Halsted Press, Div. of John Wiley & Sons, Inc., New York.

WARSHEL, A., and M. KARPLUS. 1974. Calculation of $\pi\pi^*$ excited state conformations of vibronic structure of retinal and related molecules. *J. Am. Chem. Soc.* **96**:5677.