Comprehensive Investigation of the Spectroscopy and Photochemistry of Retinals. I. Theoretical and Experimental Considerations of Absorption Spectra

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Abstract: Detailed absorption spectral studies have been carried out for the *all-trans-*, 9-*cis*-, 11-*cis*-, and 13-*cis*-retinals at 77°K and room temperature. Particular emphasis was placed on determining the number of transitions and the sensitivity of band maxima and intensities of all transitions (both ϵ and oscillator strength) to temperature. Theoretical calculations were done and transition energies and oscillator strengths predicted. The experimental and theoretical data are in good agreement particularly using 77°K absorption data. Based on the foregoing and potential energy curves arising from carbon–carbon single- and double-bond twisting, notable geometry changes are predicted to occur when cooling from 298 to 77°K. Geometric considerations are discussed for each isomer and a comparison is made among all isomers.

The purpose of this investigation was to study in detail the absorption spectroscopy and the corollary theoretical aspects of *all-trans*, 11-*cis*-, 9-*cis*-, and 13-*cis*-retinals. A following paper will consider parallel detail of the emission spectroscopy, photochemical behavior, and the corollary theoretical considerations for the same molecules. There have been earlier considerations of the room- and low-temperature spectral properties of some or all these molecules.[2-4] There also have been some theoretical considerations pertinent to the expected spectral behavior of the geometric isomers of polyenes utilizing an FEMO approach.[5-9] Experimental verification of several aspects of the theory have been made particularly with reference to the isomeric β-carotenes.[10] In addition, limited theoretical consideration of the absorption spectral properties of *all-trans-* and 11-*cis*-retinals has been made utilizing the semiempirical SCF–MO–CI method.[11-13] An experimental spectral study of the isomeric retinols (not retinals) has recently been reported[14] with particular emphasis on the mirror-image relationship of the absorption and fluorescence spectra. Patel[15] has considered the consequences of steric strain in 11-*cis*-retinal employing nmr results. Theoretical consideration of whether the retinals exist as s-cis or s-trans around the 6–7 single bond has been made.[16]

The present investigation considers an experimental investigation of all electronic transitions to ~210 nm at both room (298°K) and low temperature (77°K), including oscillator strength (*f* number) determination. These are compared with theoretical calculations of transition energies, oscillator strengths, and the effect that twisting around single and double bonds has particularly upon the transition energies. All geometric isomers of retinal noted above are considered.

Experimental Section

The *all-trans*-, 9-*cis*, and 13-*cis*-retinal were purchased from Sigma Chemical Co. and used immediately without further purification. The 11-*cis*-retinal was a generous gift of Hoffmann-La Roche Chemical Co. and was chromatographically pure. The 3-methylpentane (3-MeP) solvent was purchased from Phillips Petroleum Co. as greater than 99 mol % pure and subsequently was refluxed and distilled from Dri-Na and passed through an 18-in. column of fresh silica gel. Long-stemmed flat-faced cells with 2-mm path lengths were used in conjunction with liquid nitrogen dewars whose windows were also flat. All optical quartz was of Suprasil.

The absorption spectra were run on a Cary Model 15 spectrophotometer and were corrected for an appropriate background contribution from surface reflection, radiation scattering, and contraction upon cooling. The oscillator strengths were determined from multiple planimeter tracings of large-scale reproductions of the absorption spectra which had been empirically divided into the individual transitions assuming Gaussian band shapes. The oscillator strengths are correct within ±20%.

The preparation of all Lexan (polycarbonate) film samples of *all-trans*-retinal was accomplished in a drybox containing dry nitrogen gas. All solvents were thoroughly degassed with nitrogen gas before use. The Lexan pellets were obtained from General Electric Co. and dried by heating in an oven for 48 hr at 100°. The film-making solution was prepared by saturating boiling methylene chloride with Lexan pellets, removing the excess Lexan, and boiling the solution until it was reduced to half volume. The solution was then cooled to room temperature and mixed with the *all-trans*-retinal which had been dissolved in 3 or 4 drops of methylene chloride. This viscous mixture was spread on glass plates to a thickness of ~0.25 mm. The film was removed and spectra were determined immediately.

Theoretical Calculations. The following numerical values were used for the planar skeletal structure of the four retinal isomers: 1.36 Å for the double bond, 1.46 Å for the single bond, and 1.22 Å for the carbonyl group. The value 120° was assigned to the bond

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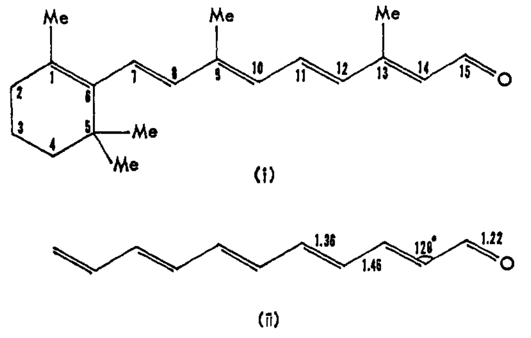

Figure 1. Structure of *all-trans*-retinal (i) and the model used for theoretical calculations (ii).

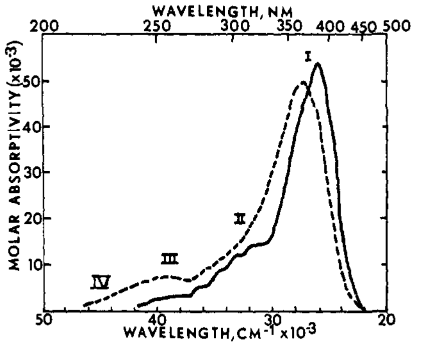

Figure 2. Absorption spectra of *all-trans*-retinal at 298 °K (– – –) and at 77 °K (—).

angles, ∠CCC and ∠CCO; Figure 1. The skeletal structure with π electrons only was taken into account. The calculation of the state energies of the four retinal isomers was carried out within the framework of the general semiempirical SCF–MO–CI method. In one calculation the ground-state energy was modified in successive iterations by minimizing the energy with respect to bond order until self-consistency was obtained using Mataga–Nishimoto approximation[17] for the electron repulsion integrals.[11] The electron repulsion integrals and β_{CC} resonance integrals were corrected through the bond order during iteration.[11] The excited-state energies were calculated using a Mataga–Nishimoto approximation for the repulsion integrals. In a separate calculation the ground-state and excited-state energies were calculated using a Pariser–Parr approximation[18] for the repulsion integrals. The β_{CC} resonance integrals and repulsion integrals were also corrected in this calculation by bond order.

For the planar molecules, the resonance integral for the nearest neighbor carbon atoms, β_{CC}^0, is treated as a parameter and adjusted to fit the calculated lowest π,π state energy (transition I) of the *all-trans*-retinal to the experimental value. The same β_{CC}^0 value was used to calculate all other state energies for *all-trans-* as well as all state energies for the *cis*-retinals. The resonance integral value for the carbonyl group, β_{CO}, in both calculations was obtained by Kon's equation[19] and was fixed in value through each of the calculations. In the present paper, the state energies for the twisted 11-*cis*-retinal around the 11–12 double bond and the 12–13 single bond were calculated using a Pariser–Parr approximation for the repulsion integral within the framework of semiempirical SCF–MO–CI without bond-order correction to explain the spectral behavior of these isomers at room and low temperatures. The resonance integral, $\beta_{CC}(\theta)$ for the twisted bond was calculated from the following equation

$$\beta_{CC}(\theta) \approx \beta_{CC}^0 \cos \theta$$

where θ is the angle of twist and β_{CC}^0 is the value for the planar structure (0° twist). The β_{CC}'s ($\beta_{C=C}$ or β_{C-C}) for all other bonds were not changed. The $\beta_{C=O}$ was obtained from Kon's equation and was not changed.

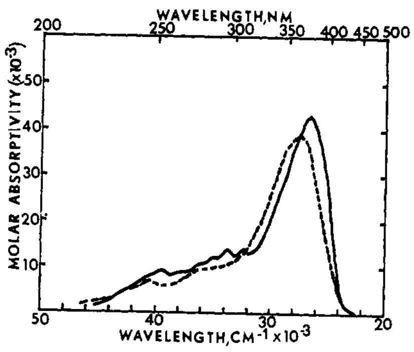

Figure 3. Absorption spectra of 9-*cis*-retinal at 298 °K (– – –) and at 77 °K (—).

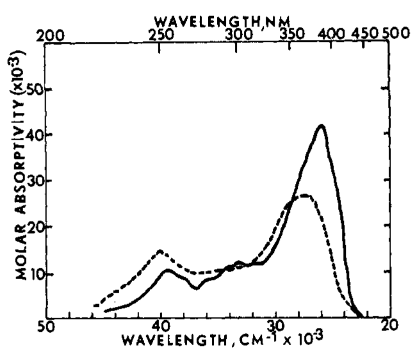

Figure 4. Absorption spectra of 11-*cis*-retinal at 298 °K (– – –) and at 77 °K (—).

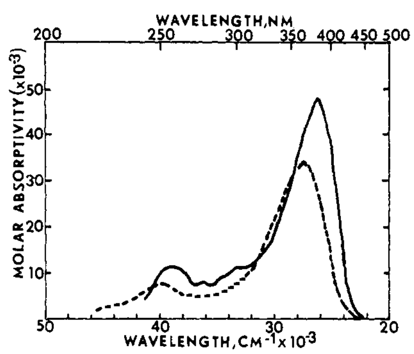

Figure 5. Absorption spectra of 13-*cis*-retinal at 298 °K (– – –) and at 77 °K (—).

Results and Discussion

Figures 2–5 show the room-temperature and low-temperature (77 °K) absorption spectra of the isomeric retinals in 3-methylpentane (at 77 °K, the solution is rigid). Table I gives a comparison of the experimental and theoretical results, including *f* numbers. The data in Table I were obtained utilizing the Mataga–Nishimoto approximation for the repulsion integrals. Spectral results predicted utilizing a Pariser–Parr approximation for the repulsion integrals for s-trans (around the 6–7 single bond) are in general agreement with those shown. That is, the first transitions are predicted to be in the same spectral region (±3 nm) and with an intensity considerably greater than all others. Also, in general, the relative order of the intensities of the other transitions are comparable to those using the Mataga approximation. All transitions except the first are predicted to be at shorter wavelengths, and transitions

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Table I. Experimental and Theoretical Transition Energies and Intensities

Compound	Transition I[a]		Δν (77–298°K)	Transition II[a]		Transition III[a]		Transition IV[a]		Transition V[a]
	298°K	77°K		298°K	77°K	298°K	77°K	298°K	77°K	
All-trans										
Theory[b]										
s-cis		384 (1.93)			285 (0.10)		270 (0.10)		233 (0.06)	
s-trans		382 (2.19)			284 (0.20)		267 (0.0)		232 (0.01)	218 (0.13)
Exptl[c]	369 (1.24) ε 50,000	384 (1.14) ε 54,000	~990	260–310 (0.26)	260–310 (0.26)	247 (0.16)	~251 (0.04)	d	~225 (0.01)	
11-cis										
Theory[b]										
s-cis		390 (1.55)			291 (0.48)		271 (0.48)		235 (0.09)	
s-trans		387 (1.86)			289 (0.24)		268 (0.25)		233 (0.03)	219 (0.18)
Exptl	363 (0.71) ε 26,400	384 (0.88) ε 41,300	~1510	260–310 (0.21)	300 (0.30)	255 (0.32)	254 (0.20)	~224 (0.07)	~225 (0.02)	
9-cis										
Theory[b]										
s-cis		390 (1.48)			292 (0.13)		272 (0.52)		234 (0.13)	
s-trans		387 (1.89)			290 (0.20)		268 (0.25)		232 (0.05)	219 (0.18)
Exptl	362 (1.04) ε 39,000	377 (0.97) ε 43,400	~1030	280 (0.19)	296 (0.36)	247 (0.11)	~252 (0.10)	~222 (0.04)	~225 (0.07)	
13-cis										
Theory										
s-cis		386 (1.75)			286 (0.15)		272 (0.20)		234 (0.07)	
s-trans		384 (2.02)			285 (0.24)		270 (0.06)		233 (0.01)	219 (0.14)
Exptl	364 (0.86) ε 34,200	380 (1.01) ε 48,000	~1080	260–310 (0.13)	311 (0.31)	251 (0.11)	~253 (0.12)	d	d	

[a] Numbers in parentheses are *f* numbers; all wavelengths in nm for transition maxima; see figures for transition assignment. [b] Theoretically calculated wavelength and *f* number data do not refer to any particular temperature; see discussion in text. [b] Absorption obtained under other conditions as follows at room temperature: CH_2Cl_2, 384, ~270, 251 nm; absolute C_2H_5OH, 383, 249 nm; $(C_2H_5)_2CO_3$, 372, 277, 246 nm; solid on fused quartz plate, 387 nm; reflectance of microcrystals, 435, 350 nm; Lexan (polyphenylcarbonate) film, 381 (300°K) and 385 nm (77°K). [d] Transition not observable.

II and III are predicted to be considerably less separated (~8 nm) than found using the Mataga approximation (and in experiment).

Data are included for both the s-cis and s-trans models around the 6–7 single bond. In general, the predicted wavelengths of the transitions are similar. However, the *f* numbers for the transitions employing the s-trans model more closely fit the experimental data. Using the model (ii) shown in Figure 1, the s-trans conformation ground-state energy is lower than that of the s-cis. Another type of calculation utilizing structure i of Figure 1 indicates a slightly lower energy for the s-cis conformation but that there is an angle of 40° between the plane of the ring and the plane of the chain.[16] However, it is known that in this type of calculation steric factors are overemphasized[20] and that small modifications in geometry may substantially influence the shape of the potential energy curve from which the stable configuration is deduced. It is quite likely to be impossible to establish the correct confirmation by theoretical calculations. In addition, the geometry is temperature dependent (*vide infra*) and, in fact, the geometry of this molecular region of the molecule may be especially sensitive to temperature changes.

Another calculation of the transition energies[13] employed both the s-trans and s-cis conformations. The energy of the longest wavelength transition (I) was uniformly predicted to be at considerably shorter wavelengths[13] (~25 nm) than found in either of our calculations and in our experiments. Furthermore, the second transition was assigned to be one in the 250-nm region.[13] Our theoretical data and experimental data, Table I and Figures 2–5, show that in fact, the second transition is in the 260–310-nm region (maximum 280–290 nm). The transition at 250–255 nm (experiment) is the third transition (Table I, Figures 2–5, and *vide infra*). Our theoretical calculations also show that the transition maxima shift to shorter wavelengths in changing from the s-cis to the s-trans model. However, the shift is less notable, Table I, than that found by others.[13] In fact, the additional blue shift found by others[13] further increases the discrepancy between their theoretical results and that of experiment.

Table II. State Energies for 11-*cis*-Retinal Twisted about the 12–13 Single Bond[a]

θ, deg	^1E_I[b]	$^1E_{II}$	$^1E_{III}$	$^1E_{IV}$
0	3.239 383	4.793 259	4.945 251	5.824 213
20	3.276 378	4.804 258	4.978 249	5.823 213
30	3.322 373	4.810 258	5.027 247	5.817 213
40	3.387 366	4.808 258	5.098 243	5.800 214
50	3.469 357	4.796 258	5.188 239	5.765 215

[a] $\beta_{C=C} = -2.5$, $\beta_{C-C} = -2.3$, $\beta_{C=O} = -2.67$ eV. [b] At each θ, first value in eV, second value in nm.

Tables II and III show the effect twisting around the 11–12 double bond and the 12–13 single bond has upon the energy difference between the ground state and

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Table III. State Energies for 11-*cis*-Retinal Twisted about the 11–12 Double Bond[a]

θ, deg	$^1E_{I}$[b]	$^1E_{II}$[b]	$^1E_{III}$[b]	$^1E_{IV}$[b]
0	3.239	4.793	4.945	5.824
	383	259	251	213
10	3.223	4.779	4.931	5.809
	385	259	251	213
20	3.175	4.737	4.896	5.762
	390	262	253	215
30	3.091	4.655	4.843	5.676
	401	266	256	218
40	2.963	4.518	4.774	5.529
	418	274	260	224
50	2.781	4.322	4.682	5.304
	446	287	265	234

[a] $\beta_{C=C} = -2.5$, $\beta_{C=C} = -2.3$, $\beta_{C=O} = -2.67$ eV. [b] At each θ, first value in eV, second value in nm.

lowest four singlet excited states of 11-*cis*-retinal. Twisting around the double bond lowers the energy difference (red shift) while twisting around the single bond increases the energy difference (blue shift). The results are general for twisting around a double bond or single bond of any of the geometric isomers. That is, for example, twisting around the 9–10 double bond of the 9-cis isomer would result in a red shift while twisting around the 10–11 single bond would result in a blue shift.

Our first consideration will be to point out that uniformly, for all isomers, the maximum of the first transition is theoretically predicted to be at longer wavelengths than found at room temperature. However, there is in general very good agreement with the experimental data determined at 77°K. Large red shifts (1000–1500 cm^{-1}) occur in the maxima upon cooling. It should be remembered that the theoretical results presume the molecules are perfectly planar. Thus, for *all-trans*-retinal, the very close agreement between theory and experiment at 77°K strongly suggests that the molecule is nearly planar at 77°K. Counter to this, the fact that at room temperature the maxima are at *shorter* wavelengths strongly indicates that there are molecules present that are twisted about *single* bonds. Twisting about a *double* bond would cause the maximum to be at *longer* wavelengths at room temperature. Thus, upon cooling from room temperature to 77°K, twisting about the single bonds is reduced to the point that all molecules are nearly planar.

The maxima of the first transition of the cis isomers are theoretically predicted to be at longer wavelengths than those of the trans isomer. At room temperature, experimentally the maxima appear at shorter wavelengths than in the *trans*-retinal. In general, this is indicative of the fact that in the cis isomers, molecules exist that are twisted about single bonds. However, certain further considerations must be made. Consequently, we will first discuss the *all-trans*- and 11-*cis*-retinals. Theoretically, the maximum of the first transition of 11-*cis*-retinal is predicted to be at a longer wavelength than that of the *all-trans*-retinal. Experimentally, at room temperature, the maximum of the 11-cis isomer is at a shorter wavelength than that of all-trans isomer, but at 77°K, the maxima are at essentially identical wavelengths. Correspondingly, the red shift when going from room temperature to 77°K is much larger for the 11-cis (~1500 cm^{-1}) than for the all-trans isomer (~990 cm^{-1}). The room-temperature data clearly indicate that in the 11-cis case, considerably more molecules are twisted about a single bond(s) or that the average angle of twist about a single bond(s) is greater than at 77°K. This is not unexpected, since in the 11-cis isomer there is an additional significant CH_3–H repulsion which is absent in the all-trans case. The near agreement between theory and low-temperature data for the maximum of the first transition does not mean that the 11-cis isomer is planar at 77°K. There still must remain some CH_3–H repulsion and thereby some nonplanarity. If twisting around the single bonds were eliminated, then a red shift would occur. Yet, since coplanarity is still impossible, some double-bond twisting must be present. Thus, the large red shift for the 11-*cis*-retinal could result from a large decrease in single-bond twisting with some double-bond twisting remaining or a decrease in single-bond twisting and an increase in double-bond twisting. Our calculations indicate that over the first ~20° of twist, the ground-state energy increase is about the same for a single- and double-bond twist (the increase is slightly more for double-bond twisting). Beyond 20°, the ground-state energy rises more rapidly for double-bond twisting. Thus, the final situation must be one in which there is both double-bond and single-bond twist and at such angles as to minimize the total energy.

Additional consideration of the data pertinent to the 9-*cis*- and 13-*cis*-retinals is in harmony with the foregoing conclusion. Again, the theoretically predicted maxima are at longer wavelengths than found experimentally at room temperature, indicating twisting about a single bond(s). Upon cooling to 77°K, there is a notable (~1050 cm^{-1}) red shift, indicating reduction in the single-bond twisting. Note that the maxima of the first transition for the 9-, 11-, and 13-cis isomers at room temperature are very nearly the same. Only H–H repulsion is expected for the 9-cis and 13-cis cases compared with CH_3–H for the 11-*cis*-retinal. If twisting around the single bond was the sole source of steric relief, the maximum for 11-cis should have been at considerably shorter wavelengths than for the 9- and 13-*cis*-retinals, which it is not. Thus, some double twisting must be present in 11-*cis*-retinal at room temperature which would cause a compensating red shift and move the maximum to very near that of the 9- and 13-cis cases. This conclusion for the situation in the 11-*cis*-retinal is the same as that obtained from the *all-trans*- and 11-*cis*-retinal comparison (*vide supra*). Particularly for 9-*cis*-retinal, cooling to 77°K still results in the maximum being at shorter wavelength than predicted. Thus, although there is a reduction in single-bond twist upon cooling, it is not complete. This is not surprising in view of the existence of some H–H repulsion. The spectral data are compatible with the premise that there is very little if any double-bond twisting in either the 9- or 13-cis isomers.

It is also important to note that theory predicts the first transition to be the strongest one (largest *f* number). This is in agreement with experiment, Table I, where comparison should be made with the 77°K data, where the molecules would be the most nearly planar (this agreement also occurs at room temperature). Furthermore, the ordering of the intensity (*f* numbers) of the first transition (I) of the isomers is correctly pre-

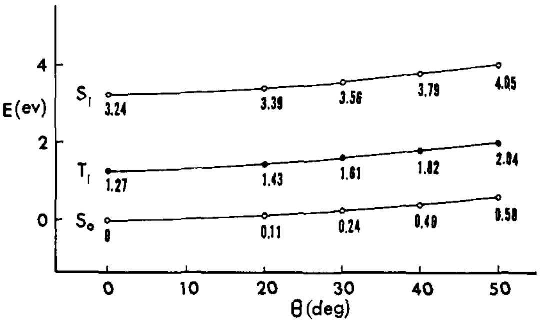

Figure 6. The potential energy curves of 11-*cis*-retinal twisted around the 12–13 single bond.

dicted by theory, Table I, at 77 °K

all-trans > 13-cis > 9-cis ∼ 11-cis

For the remainder of the transitions, the theoretically predicted spectral locations are in good agreement with experiment; Table I. Also, for the remaining transitions, the *f* numbers calculated utilizing the s-trans model around the 6–7 bond are in good agreement with experiment. The agreement utilizing an s-cis model is generally noticeably poorer regarding the *f*-number calculation.

It is also worth noting the relatively large increase in molar absorptivity (ϵ) of the first transition upon cooling from room temperature to 77 °K; Table I. The change is particularly large for the 11-*cis*- and 13-*cis*-retinals. A similar result has been noted by others.[2] However, it should be pointed out for the *all-trans*- and 9-*cis*-retinals that despite an increase in ϵ at the −196° compared to room temperature, the *f* number stays approximately the same; Table I.

Another important point concerns the assignment of the so-called cis band. This band was recently assigned as the one in the 265–300-nm region.[4] This was based on a model in which there was a 90° twisting around the 10–11 single bond of some molecules. We shall return to a consideration of other aspects of this approach and its results shortly. Our theoretical results, utilizing the s-trans model, show that it is for the band in the 250-nm region that the intensity is weakest for the trans isomer. Among the cis isomers, this band is weaker the less central is the double bond about which twisting must occur to make the appropriate cis isomer. This is true whether the model used is s-cis or s-trans around the 6–7 bond and for both the Mataga–Nishimoto and Pariser–Parr approximations. FEMO theory and group theory also predict that the more centrally located is the cis bond, the more intense will be the absorption associated with the cis band.[5] This has been confirmed for several molecules.[10] Thus, the band would be predicted to be very weak or absent in the all-trans isomer, quite weak in the 13-cis isomer, and considerably more intense in the 9- and 11-*cis*-retinals. These theoretical predictions are parallel to those found using our theoretical approach. Furthermore, the experimental results at −196° parallel those predicted by theory. Thus, we assign the band in the 250-nm region as the cis band.

We shall now return to other aspects of the model employing the twisting of some molecules by 90° around the 10–11 bond to explain the spectrum of the 11-*cis*-retinal.[4] Twisting by 90° presumably gives two independent moieties which both absorb in the 250-nm region.[4] There are several points to be made. First and of overwhelming importance is the fact that a transition in the 250-nm region is predicted for the 11-*cis*-retinal where the model employs a *planar* structure; Table I. Furthermore, all of the other transitions found, including one at higher energy (∼225 nm), are predicted based on the same model. The transition in the 250-nm region is predicted with varying intensity for all other cis isomers and with very low intensity for the all-trans case; Table I. Although there are deviations from planarity in 11-*cis*-retinal as discussed above, the principal spectral features such as the general number, location, and intensity of the transitions arise utilizing a planar model. Twisting is required to explain more subtle spectral features (*vide supra*). Secondly, energy is required to twist around a single bond in the ground state; Figure 6. In addition, there is experimental verification of this.[21] Therefore, there will be a Boltzmann distribution of molecules at various angles and, in fact, the number of those at 90° will be extremely small because of the exponential dependence. Thus, on the basis of the model chosen,[4] there would be absorption at all wavelengths between the lowest energy band (∼364 nm at 298 °K) and the band at ∼250 nm (at 298 °K). In fact, the intensity in the ∼250-nm region should be very weak and that toward ∼364 nm stronger because of the population expectation. Clearly the experimental data are not in agreement with this. Even if the β value of the bond is equal to zero, theory shows that the degenerate transitions will split according to the degree of the interaction between the two chromophores and the degeneracy removed. Thus, bands would exist not at the wavelength anticipated but at both longer and shorter wavelength.

In view of the preceding discussions, we agree with Patel[15] that steric strain in 11-*cis*-retinal is relieved by twisting around the 12–13 single bond. However, all of the spectroscopic results and theoretical comparison indicate that twisting also occurs around the 11–12 double bond to some extent. This is not in agreement with Patel.[15]

Earlier work[2] indicated that in cooling to 88 °K it was as though steric hindrance was relieved in the 11-cis isomer. Fortuitously, the result does appear this way. However, it is actually the reduction in single-bond twisting (red shift) with residual or increased double-bond twisting (red shift) that accounts for the final result (*vide supra* for a discussion of the 11-cis and other retinals).

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