POSSIBLE INFLUENCE OF A LOW-LYING "COVALENT" EXCITED STATE
ON THE ABSORPTION SPECTRUM AND PHOTOISOMERIZATION OF 11-*CIS* RETINAL[*]

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The anomalous temperature dependence of the absorption spectrum and photochemical isomerization efficiency of 11-*cis* retinal is analyzed in terms of an equilibrium mixture of distorted 12-*s-cis* and distorted 12-*s-trans* conformers with the latter increasingly populated at lower temperature and/or greater solvent polarity. Inclusion of all possible singly and doubly excited configurations in the PPP formalism predicts a conformationally variant level ordering in that all 12-*s-cis* conformations have a lowest excited "^1B_u"-like singlet state whereas the majority of the 12-*s-trans* conformations have a lowest excited "^1A_g"-like singlet state.

Although 11-*cis* retinal, the chromophore of the visual pigment in vertebrate rods, has been the subject of numerous investigations, certain of its properties are not completely understood. Among these are the temperature dependence of its UV absorption spectrum and photochemical isomerization efficiency. In this communication, we describe a low-lying excited state that is predicted to exist in the neighborhood of the canonical strongly absorbing π, π^* state of polyene-like systems and examine its possible importance in producing the anomalous behavior of 11-*cis* retinal.

Although the Pariser—Parr—Pople (PPP) semi-empirical formulation of SCF LCAO MO theory with singly-excited configurations has been the standard method for interpreting the spectra of polyenes and related systems, recent experimental [1—3] and theoretical [4,5] results demonstrate that doubly-excited configurations must be introduced to obtain the correct relative ordering of "ionic" and "covalent" type

states. In particular, it has been shown theoretically that in linear polyenes like octatetraene, a forbidden excited $^1A_g^-$ state lies in the neighborhood of the strongly allowed ^1B_u state and experimentally that in diphenyloctatetraene [1,2] and undecapentaene [3], the $^1A_g^-$ state is the lowest excited state. In spite of the inability of the π-electron theory at its present level of refinement to predict unequivocally which of the two states ("$^1A_g^-$"-like or "^1B_u"-like) is lower in a system like retinal, it is important to consider the possible effects of the revised energy level scheme on the absorption spectrum and the photochemistry. For this purpose, we apply the calculational method described previously [4] to the retinal isomers. All double excitations are included in the configuration interaction treatment, in addition to the usual single excitations. Higher excitations (triple, quadruple) can be neglected for simplicity, since studies of model polyenes (butadiene, hexatriene) have shown that they produce little change in the relative ^1B_u and $^1A_g^-$ positions, though they do lower both by an amount that is approximately equal to the lowering of the ground state by the double excitations; the latter effect is compensated for by using the uncorrelated ground state energy.

In fig. 1 we show the level ordering obtained for 11-*cis* retinal as a function of the torsional angle
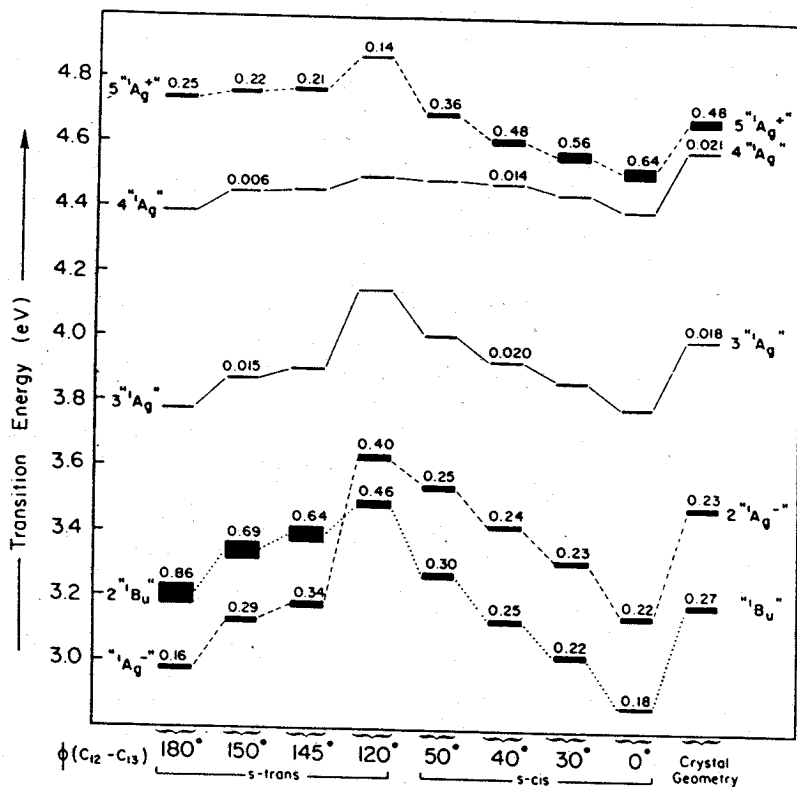
Fig. 1. The 11-*cis* retinal π-electron excitation energies as a function of the torsional angle ϕ_{12-13} from PPP calculations with all 36 single and 666 double excitations; the transition energies are relative to the uncorrelated ground state (see text); angles are defined such that planar-*s-cis* is 0°; the remaining polyene chain is planar-*trans* with the exception of the C_6–C_7 bond which is *s-cis* (45°) and the C_{11}–C_{12} bond which is planar-*cis*; standard bond lengths were assumed: $R_{C=C}$ = 1.35 Å, R_{C-C} = 1.46 Å; $R_{C=O}$ = 1.22 Å; for the crystal geometry, the bond lengths and angles were taken from ref. [8].

ϕ_{12-13}; the transition energies are given relative to the uncorrelated ground state (see above) and the states are labelled "^1A_g" or "^1B_u" according to their relation to the corresponding states of the analogous symmetric polyene. The dependence of the levels on the ϕ_{12-13} angle is of interest because it has been predicted by recent calculations [6,7] and confirmed by NMR in solution [7] that 11-*cis* retinal has two conformations with nearly the same energy — one is a distorted 12-*s-cis* conformation with $\phi_{12-13} \approx 40°$ and the other is a distorted 12-*s-trans* conformation with $\phi_{12-13} \approx 150°$; the crystal structure has ϕ_{12-13} = 41° [8]. From the NMR measurements [7] the *s-trans* conformer appears to be slightly more stable in a polar solvent ($\approx$ 1 kcal); in a non-polar solvent the energy difference may be even smaller [9]. Thus, one

would expect both *s-cis* and *s-trans* to be populated in solution with *s-trans* becoming more important, particularly in a polar solvent, as the temperature is lowered.

What is striking about fig. 1 is that there is a "crossing" of the two lowest singlet π, π^* excited states (the "$^1A_g^-$" and "^1B_u" levels) in 11-*cis* retinal as the molecular geometry changes from an *s-cis* to an *s-trans* conformation; that is, the "^1B_u" state is calculated to be lower in *s-cis*, while the "$^1A_g^-$" state is lower in *s-trans* for angles greater than about 140°. The oscillator strengths, which are indicated schematically in the figure by the width of the line corresponding to each level (the value is given above the line), are seen to be significant for both levels because of the break-down of the molecular symmetry by the

aldehyde group. In the single-excitation calculation, the 2 "$^1A_g^-$" state remains allowed but is located very near to the 5 "$^1A_g^+$" state of fig. 1; the latter is the state usually associated with the well-known "cis band" of retinal and other carotenoid pigments. The two other "^1A_g" states (labelled 3 "^1A_g" and 4 "^1A_g" in the figure) are missing in the single-excitation calculation; however, their position is not known experimentally because they are predicted to be almost forbidden and, therefore, not to contribute significantly to the observed spectrum.

The effect of temperature on the absorption spectrum of 11-cis retinal was described by Wald and his co-workers in 1959 [10−12] who observed that the oscillator strength of the dominant absorption at 3.30 to 3.40 eV increases markedly on cooling; by contrast, for all-trans retinal and the "unhindered" cis isomers (9-cis, 13-cis) there appeared to be little or no change in the oscillator strength with temperature. Sperling and Rafferty [13] have shown that upon cooling an EPA solution of 11-cis retinal from 295 K to 77 K, the oscillator strength of the main absorption band increases by a factor of 1.4 (f_{77}/f_{295}) while the lower intensity band at 4.90 eV (the "cis band") decreases by a factor of ≈ 0.5. Similar measurements in non-polar solvents by Sperling [14] and Becker et al. [15] give $f_{77}/f_{295} = 1.2$ and $f_{77}/f_{295} = 0.65$ for the 3.40 and 4.90 eV bands, respectively, suggesting that the temperature effect is slightly less pronounced in non-polar solvents. Although the band maxima also appear to shift to the red upon cooling, correction for the solvent contraction indicates that the intrinsic shift is small. The band width at half height of the main band in EPA decreases by a factor of 0.7 upon cooling to 77 K, while the band width for the "cis band" appears to remain constant [13,14].

As has been suggested recently [7,16,17], the equilibrium between the 12-s-cis and 12-s-trans conformers of 11-cis retinal offers a possible explanation of the anomalous temperature dependence of its principal absorption; that is, since the oscillator strength of s-trans is calculated to be much larger than that of s-cis (see fig. 1), a temperature dependent equilibrium between the two forms with s-trans more stable would produce the observed increase in oscillator strength with decreasing temperature. However, there is a difficulty [17] with this argument when based on PPP

calculations including only single-excitation configuration interaction; namely, the "^1B_u" state of the s-trans conformation is calculated to be significantly higher in energy than that of the s-cis conformation so that a large blue-shift is predicted, in disagreement with experiment (see above). From fig. 1 it is clear that the inclusion of double excitations partly counteracts this shift if the "^1B_u" and "$^1A_g^-$" states together make up the very broad absorption band of 11-cis retinal. This is a reasonable hypothesis, since the two transitions are calculated to be within 0.2 to 0.25 eV of each other, while the observed band has a width of 0.6 to 0.8 eV; the actual width and the complete diffuseness of the band are almost certainly due in part to vibronic effects, in accord with Franck−Condon factor calculations [17]. An additional element in the smallness of the band shift with temperature is the anharmonicity of the ϕ_{12-13} torsional potential [7,17], which leads to a less distorted molecule at lower temperature*. The dependence of the temperature effect on solvent polarity can be understood from the difference in the dipole moments of the 12-s-trans and 12-s-cis conformers. An INDO calculation yields 4.53 D for 12-s-trans and 3.34 D for 12-s-cis, suggesting a greater stability of the former relative to the latter in a polar solvent.

Another aspect of the spectrum that is significantly affected by the inclusion of double excitations is the absorption in the region of the "cis band". In the single-excitation calculation, two allowed transitions of comparable intensity (the "$^1A_g^-$" and "$^1A_g^+$" bands) occur in the region 4.5−5.0 eV. The sum of their calculated oscillator strengths is nearly equal to that of the "^1B_u" transition, in disagreement with experiment. Moreover, the two transitions result in a broader "cis band" than is actually observed. All of these difficulties are removed if the "$^1A_g^-$" state is in the neighborhood of the "^1B_u" state, in accord with the calculations including double excitations.

Although not specifically connected with the states under consideration, it is important to point out that 11-cis retinal in solvent glasses at 77 K clearly shows a weak absorption in the range 3.8−4.3 eV; in non-polar solvents, the band maximum is at 4.1 eV. In

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* In this sense, a part of the temperature effect arises from an increased planarity at lower temperature, in accord with the original suggestion of Wald [12].

contrast to the other retinal bands, this band shows some vibrational structure with a spacing of approximately 1500 cm^{-1}. None of the π-electron calculations (including single or single and double excitations) predict a band in this region. Consequently, the band might well be due to an n, π^* or other σ, π^* transition[*] whose more localized nature might protect it from the vibronic effects [17] leading to the diffuse character of the π, π^* bands.

As shown by Kropf and Hubbard [20], the temperature dependence of the quantum efficiency of the photoisomerization of 11-cis retinal is anomalous. Their results for the retinal isomers are given in table 1. For all-trans, 9-cis, and 13-cis the quantum efficiency decreases with decreasing temperature as would be expected from the presence of a barrier to the isomerization; for 11-cis, the quantum efficiency is seen to *increase* as the temperature is lowered. If a significant fraction of the photoisomerization were to proceed through the singlet manifold (the relative contributions from the singlet and triplet manifolds have not been determined), the 12-s-trans/12-s-cis conformational equilibrium in 11-cis retinal might explain the anomalous behaviour. Since the importance of double excitations in the "$^1A_g^-$" state leads to a geater degree of "bond-order reversal" than there is in the "^1B_u" state, the "$^1A_g^-$" is expected to have a significantly lower barrier to isomerization. Consequently, low temperature stabilization of the 12-s-trans conformer, in which the "$^1A_g^-$" state is the lowest excited singlet $\pi\pi^*$ level[**], could account for the increased photoisomerization efficiency on cooling. Further, no such effect would be expected in the other isomers which have only one dominant conformation.

The arguments on which this communication is based are speculative, in part because the study of a molecule as large as 11-cis retinal necessitates the use of a relatively crude theoretical model. However, the fact that a single refinement of the model permits it to explain several of the anomalous properties of 11-cis retinal appears to us to justify a presentation

of the results. A test of their validity by suitable experiments is now in order.

Table 1
Quantum efficiencies (γ) for retinal isomer photoisomerization[a]

Reaction[b]	$\gamma(25°C)$[c]	$\gamma(-65°C)$[c]
all-trans $\xrightarrow{hv}$ cis	0.06–0.2	0.002–0.005
9-cis $\longrightarrow$ trans	0.5	0.25
11-cis $\longrightarrow$ trans	0.2	0.6
13-cis $\longrightarrow$ trans	0.4	0.1

a) All data are from ref. [20].   b) Excitation wavelength is 365 nm.   c) In hexane.

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* INDO AFAOS calculations [18] give a level ordering for 11-cis retinal of π, $\pi^* <$ n, $\pi^* < \sigma$, $\pi^* < \pi$, π^* [19].
** Preliminary all-valence electron calculations indicate that the n, π^* singlet state, which in principle could also participate in the photochemistry and lead to significant intersystem crossing, is above the "^1B_u" π, π^* state [19].