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CALCULATED MOLECULAR STRUCTURES AND ELECTRONIC SPECTRA OF THE GEOMETRIC ISOMERS OF A MODEL CAROTENOID MOLECULE, 6, 11-DIMETHYLHEXADECAHEPTAENE[1]

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Abstract—The molecular structures and the electronic spectra of the geometric isomers of a model carotenoid polyene, 6, 11-dimethylhexadecaheptaene, were calculated. It was concluded that solvent effects and conformational isomerization must be taken into account in order to satisfactorily explain the observed spectra. Molecular structures were calculated using molecular mechanics (MM2), and electronic spectra using the VESCF-MO-CI method including all singly-excited configurations. A method based on the calculated and observed spectra of simple linear polyenes was devised to estimate the solvent effects.

Carotenoids are naturally-occurring modecules whose chromophores have a polyisoprene structure and contain five to fifteen double bonds. It was found that when a pure carotenoid compound was dissolved in a solvent and exposed to light, it was often converted to a mixture of stereoisomers. These were believed to be *cis-trans* isomers about one or more of the conjugated double bonds. All *cis-trans* isomers of the same molecule are said to belong to a *stereoisomeric set.* They can be separated by chromatographic methods. The most stable isomer is the all-*trans* one.

Much experimental work has been done on the electronic spectra of carotenoids.[3,4] It was observed that the spectrum of an all-*trans* carotenoid exhibits only one absorption of high intensity (which shows vibrational fine structure) in the visible or near UV region. When one or more *cis* double bonds were present, the intensity of this absorption became weaker and the wavelength shifted slightly to the blue. In addition, a second, weaker absorption, the so-called *cis*-peak, appeared at about 50–150 nm below the first one. With some isomers, the blue shift of the first transition and its decrease in intensity relative to the all *trans* isomer were particularly pronounced. It is believed that such isomers contain one or more "hindered" *cis* bonds, such as exists in 2-methyl-1, 3-*cis*-5-hexatriene. These observations were explained on the basis of the molecular geometry. An all-*trans* molecule has a chromophore which belongs to the symmetry group C_{2h}, for which transitions between the ground state and states belonging to symmetry A_g are forbidden. A *cis* conformation changes the point group of the chromophore into C_s, or C_{2v}, and some transitions become allowed, one of them being the *cis*-peak. The decreasing intensity and the blue shift were thought to be due to the nonplanarity introduced by the *cis* bond, which would decrease the conjugation of the π system.

However, experience and preliminary calculations[5] indicated that the first spectral transition would show a red rather than a blue shift upon conversion of a trans linkage to a *cis* one, and the transition probability does not decrease very much. In order for calculations to be able to reproduce the observed spectral change, the molecules must be severely distorted from planarity upon introduction of a *cis* bond, and preliminary calculations of geometry indicated that this would not be true in most cases. It became clear then, that factors other than the geometry of the carotenoid molecules must be taken into consideration before their electronic spectra can be satisfactorily explained. Two such factors came immediately into mind, namely the existence of *s-cis* conformers in the equilibrium mixture, and the solvent effect which causes a red shift of the solution spectrum relative to the vapor phase. Although there exist many experimental data in the literature, no theoretical calculations on an entire stereoisomeric set of any carotenoid have been published, and most of the calculations that do exist for individual carotenoid molecules took neither the solvent effect nor the existence of conformers into consideration. We therefore undertook this study on a model carotenoid molecule in order to assess the importance of these factors and to gain a better understanding of the electronic spectra of this class of compounds.

Molecular structure

Earlier studies[6] on the energies and structures of some small polyenes using molecular mechanics (MMPI force field, 1973) suggested that some *s-cis* conformers would be important in polyenes with methyl substitution. The molecular mechanics method used in the present work is similar to that described in detail earlier.[7] It It is now known that the van der Waals hardness used for hydrogen in the 1973 force field (MMI and MMPI) was somewhat too large, and calculations in this study are based on a better, and more modern force field (MM2).[8] The reduced "hardness" of hydrogen atoms in this force field led to small changes in the geometries of polyenes, compared with earlier calculations.[6,7] The C–C–C angles do not tend to open quite as much with this force field, and there is now a greater tendency for the molecule to remain planar. But the largest difference between the two force fields is in the calculated energies for *s-cis* vs *s-trans* isomers. A somewhat more accurate experimental rotational profile for butadiene is now available,[9] and especially important from a practical point of view, an experimental value for the corresponding equilibrium in isoprene has now been reported.[10] It is known that the *s-cis*-isoprene has an energy only about 1.3 kcal mol^{-1} above that of the *s-trans*-isomer. Earlier this value was assumed to be about 2.3 kcal mol^{-1}, which is obviously not very accurate. These revised experimental quantities permitted us to construct a more accurate function for torsion about a π bond as a function of bond order, similar to that described for MMPI.[7] The equation for the energy as a function of torsional angle reads

$$E = -\frac{1}{2}\beta_o S_{ij} p_{ij} f\,(1 - \cos 2\omega).$$

In Table 1 are given the calculated relative energies using force field MM2 for the different isomers and conformers of butadiene, hexatriene, and a few methylated derivatives. The rotational barrier from the *s-trans* ***ated derivatives. The rotational barrier from the s-trans*** to the *s-cis* conformation for butadiene is calculated to be 7.7 kcal mol^{-1} compared to an experimental value of 7.2 kcal mol^{-1};[9] for isoprene, it is calculated to be 5.7 kcal mol^{-1}.

It can be seen from the data in Table 1 that in butadiene and hexatriene, conversion of a *s-trans* conformation to a *s-cis* conformation raises the energy by about 2.4 kcal mol^{-1}, while in isoprene and 2-methylhexatriene a similar conversion raises the energy by only 1.2 kcal mol^{-1}. The energy difference in the latter case is still sufficient so that there is not much of the *s-cis* isomer present in the equilibrium. However, the situation may be different if there are additional forces at work. As was discussed earlier,[6] while a methyl group at carbon 2 in *trans*-hexatriene exerted no effect other than what one would predict from the analogous structure in isoprene, if the methyl was at carbon 3 (which was referred to as "flanked"), the *s-cis* conformation was stabilized relative to the *s-trans*, and now lies only 0.3 kcal mol^{-1} above the latter. For a "hindered" methyl group (as in 2-methyl-*cis*-hexatriene), the *s-cis* isomer (cCt) is almost equal in energy to the *s-trans* (*tCt*). Consequently, molecules which contain methyl groups which are "flanked" or "hindered" have appreciable amounts of conformations other than the simple *s-trans* present in the equilibrium mixture at room temperature. We would therefore expect that the equilibrium conformational mixture of any carotenoid would include a fair amount of *s-cis* conformers. The equilibrium concentrations of conformers can be calculated using the Boltzman distribution law once the relative energies of these conformers are obtained. It can also be seen that these molecules are all nearly planar, except in those where there are adjacent *cis* (or *s-cis*) bonds.

Electronic spectra

As shown earlier,[11,12] the VESCF–CI method including all doubly-excited configurations yields excellent predictions regarding electronic spectra for conjugated polyenes, even when they are nonplanar. Unfortunately, calculation of the necessary matrix elements for the inclusion of these doubly-excited configurations in larger molecules becomes impossibly time consuming. This is because the order of the CI matrix increases by approx. m^2 if only singly-excited configurations are used, but by about $m^4/2$ if doubly-excited configurations are included (where m is the number of double bonds). It is clear that except for polyenes containing not more than about five double bonds, inclusion of all doubly-excited configurations in the CI matrix is too time consuming to be practical at present. Yet it is known that the lower excited states in polyenes contain large fractions of doubly-excited configurations.[11-14] Earlier studies of the effects of omitting various groups of doubly-excited configurations by truncation of the CI matrix at different energy levels showed that the results did not seem to converge at any clear-cut point.[15] On the other hand, if all doubly-excited configurations are omitted (calculation S), the results obtained show a definite correlation with those obtained including all doubly-excited configurations (calculation D). In the present study, we therefore decided to use calculation S while taking the following observations into account:

(1) When the same value of the parameters γ_{11}, β_0, etc. are used, the predicted energies for corresponding transitions using calculations D are about 0.4 eV higher than obtained using calculation S. This discrepancy can be corrected by choosing different values of β_0 for the two types of calculations, while keeping the other parameters the same. Therefore in the S calculations, we used $\beta_0 = -2.733$ eV while in the D calculations β_0 was -2.5 eV. Other parameters were given in earlier papers.[11,12]

(2) For molecules belonging to symmetry groups C_2 or C_{2v}, the first excited state with A_g symmetry lies very close to that with B_u symmetry (comprised mostly of $V_{1,-1}$.[16]). It contains a large percentage of doubly-excited configurations and is not predicted by calculation S. Since transition to it from the ground state is forbidden, calculation S sufficies for our purpose. For unsymmetrical molecules, the combination of the first two transitions predicted by D can be represented by the first transition from S. Since experimentally only the combination of the two can be seen in the UV spectrum, calculation S also serves our purpose here.

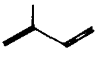
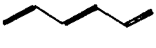
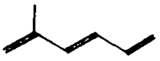
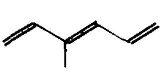
(3) The combination of the states comprised mostly of $V_{1,-2}$ and of $V_{2,-1}$ from calculations S represents the state comprised of almost equal fractions of $V_{1,-2}$ and $V_{2,-1}$ predicted by calculation D. This is the *cis*-peak. The combination of the states comprised mostly of $V_{1,-3}$ and of $V_{3,-1}$ from calculation S represents the state which consists of almost equal fractions of $V_{1,-3}$ and $V_{3,-1}$ predicted by calculation D. There are states in between those mentioned above that are predicted by calculation D but not by calculation S. These states contain large fractions of doubly-excited configurations, hence have near-zero oscillator strengths.

(4) The oscillator strength values predicted by calculation D are lower than those predicted by calculation S. Since we are going to compare the transition probabilities on a relative basis, no correction will be used to scale down the oscillator strength values.

From the above observations, we conclude that the lowest energy transition and the transition corresponding to the *cis*-peak can be correctly predicted by calculation S. It should also be pointed out that the VESCF–CI method used here worked well for nonplanar molecules as well.[12] It predicted the spectra correctly for molecules with nonplanarity up to 60°. When two conformers are present in equilibrium, the observed spectrum agrees with the weighted spectrum of the two.[12]

Next, since the available spectroscopic data on large molecules are for solutions, we need a procedure to allow for solvent effects. It is known that the $\pi \rightarrow \pi^*$ transition displays a red shift when the molecules are brought from vapor phase into a solution. When both the solvent and solute molecules are nonpolar, the frequency

Table 1. Relative steric energies and geometries of butadiene, hexatriene, and their methylated derivatives[a]

Molecule		ΔE (kcal)[b]	1234[c]	2345[c]	3456[c]
	t	0	180.0	-	-
	c	2.33	180.0	-	-
	t	0	-179.9		
	c	1.16	- 0.5		
	tTt	0	180.0	180.0	180.0
	cTt	2.43	180.0	180.0	180.0
	cTc	4.98	180.0	180.0	180.0
	tCt	2.54	180.0	180.0	180.0
	cCt	5.97	- 44.9	- 5.2	178.4
	cCc	8.58	- 38.5	- 7.02	- 38.5
	2-Me tTt	0	180.0	180.0	180.0
	cTt	1.23	180.0	180.0	180.0
	tTc	2.53	180.0	180.0	180.0
	cTc	3.79	- 8.0	179.8	- 8.3
	tCt	5.02	-157.9	5.9	-177.5
	cCt	4.94	- 44.5	- 6.8	178.3
	tCc	7.69	159.2	- 8.5	- 44.7
	cCc	7.34	- 38.0	- 8.6	- 38.0
	3-Me tTt	0	-169.2	18.5	179.3
	cTt	0.32	- 12.9	-179.5	179.6
	tTc	3.01	-173.0	178.4	- 43.1
	cTc	3.81	- 17.7	-180.0	- 44.1
	tCt	0.40			
	cCt	2.57	- 45.5	- 5.0	177.8
	tCc	3.57	171.6	- 7.0	- 45.7
	cCc	5.14	- 38.2	- 6.8	- 40.3

a) Capital letters (C, T) refer to configuration (Cis, Trans) about double bonds, small letters refer to conformation about single bonds.

b) Relative to the most stable conformation and isomer.

c) Sign of angle A-B-C-D: When looking through B toward C, if D is counter-clockwise from A, negative. Of course, each compound contains an equal amount of the mirror image.

shift was shown by Bayliss[17] to follow the expression

$$\Delta\nu = 10.7 \times 10^9 \frac{f(n^2-1)}{\nu a^3(2n^2+1)}$$

where f is the oscillator strength; n, the refractive index of the solvent; ν, the transition frequency, and a the radius of the cavity created by the solute molecule. With many small polyenes, both vapor phase and solution data are available. The solvent shifts can be calculated and used as estimates for similar systems. For larger polyenes, however, the amount of solvent shift from the vapor phase spectrum is not known experimentally, although the shift was found to increase as the refractive indices of the solvents increased.[18] Yet this knowledge is essential if one wishes to make a meaningful comparison between the calculated and the solution spectra. Ideally, the Bayliss equation could be used to supply this information. In practice, there are two major difficulties with the application of this equation. First, the accuracy of the assumption of a spherical cavity varies with the nature of the system under study. Second, apart from the first assumption, there is no good way of assigning a value to a. We have therefore tried to find an empirical relationship between $\Delta\nu$ and some measurable or calculable variables.

A VESCF–CI calculation including all singly-excited configurations was carried out for ethylene and for polyenes containing up to 11 double bonds using structures from MM2 calculations, and the lowest energy transitions are shown in Table 2. Also shown are the observed vapor and solution spectra. Since the solvent shifts appeared to increase with the number of conjugated double bonds m (or with the oscillator strength f) in molecules with $m = 1$ to 4 for which experimental data are available, a simple relationship between $\Delta\lambda$ and m (or between $\Delta\lambda$ and f) seemed likely to exist. We therefore plotted $\Delta\lambda$ values vs m and then vs f, where $\Delta\lambda$ was taken to be equal to the observed solvent shift when it was known, and to be ($\lambda_{\text{solution}} - \lambda_{\text{calc}}$) if the vapor phase data were not available. In each case there appeared to exist a nearly linear relationship. It should be noted that in the long wavelength region a small energy change results in a large difference in wavelength. Thus, although the $\Delta\lambda$ values in Table 2 range from 8 to 51 nm, in terms of energy difference, they correspond to 0.23 eV and 0.34 eV respectively. A solvent shift of about 50 nm when the transition energy is about 3 eV is therefore not an extraordinary amount as it may at first appear to be. Since the oscillator strength f will be different for different geometric isomers and conformers, while νa^3 will not be expected to change much for a polyene with a given m, it seems logical to calculate $\Delta\lambda$ from f. The empirical formula found is: $\Delta\lambda\ (\text{nm}) = 12.9f - 6.6$, eqn (1). For f smaller than 0.51, $\Delta\lambda$ will be assigned a value of zero.

It should be noted that a study[19] of the spectrum of α,ω-diphenyloctatetraene in different solvents showed that while the allowed transition depends on the refractive index of the solvent in the way described by the Bayliss equation, the energy of the forbidden transition which lies near the allowed one stays the same in different solvents. This is also consistent with the Bayliss equation, which predicts no shift when f is zero. It seems likely then, that eqn (1) can also apply to the second

Table 2. Calculated and observed electric transitions of ethylene and the simple all *trans* conjugated polyenes

m	Calculated			Observed			
	Vapor		Solution[g]	Vapor		Solution	
	λ nm	(f)	λ nm	λ nm	(f)	λnm	(f)
1	163	(0.62)	164	170[a]	(17,100)		
2	209	(1.12)	217	209[b]		217[c]	(21,000)
3	248	(1.58)	262	244[d]		257[e]	(42,000)
4	282	(2.02)	302	280[f]		302[f]	
5	311	(2.42)	336	-		334[e]	(121,000)
6	335	(2.79)	365	-		364	(138,000)
7	356	(3.14)	390	-		390[e]	
8	373	(3.48)	411	-		410[e]	(108,000)
9	388	(3.82)	431	-		-	
10	399	(4.15)	446	-		447[e]	
11	410	(4.49)	461	-		-	

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[g] Corrected from vapor data by adding a solvent shift calculated by equation 1.

higher energy $\pi \rightarrow \pi^*$ transitions, for which no adequate experimental information about the solvent shift exists.

Results and conclusions

With the calculational methods chosen and established, we calculated the geometries and electronic absorptions of all of the mono-*cis* isomers of compound 1 (6, 11-dimethylhexadeca-2-*cis*, 4-*trans*-6-*trans*-8-*trans*-10-*trans*-12-*trans*-14-*cis*-heptaene) and some of their conformers. Only those conformations that are expected to have conformational energies of 2 kcal mol^{-1} or less (by analogy with the results given in Table 1) were included. Once the conformational energies were calculated, the percent population of each conformer at room temperature was determined by the Boltzmann distribution. This molecule was chosen as a reasonable size model, which contains a chromophore of the same size as a typical carotenoid molecule. The electronic spectrum of each conformer was then calculated, and the weighted average was taken to be the predicted spectrum of the equilibrium mixture at room temperature.

The calculated values for the first two absorption bands of the various conformers of each isomer and their weighted average are presented in Table 3. Solvent shifts were obtained using their calculated oscillator strengths and the $\Delta\lambda$ vs f relation given by eqn (1). The geometries of these molecules are omitted from Table 3 for simplicity. It suffices to say that the main features agree with what would be expected for our study on the geometry of small polyenes shown in Table 1.[12]

The results show that when the *cis*-isomers are of the unhindered type, the calculated vapor phase spectra show a red shift of the first transition from the all-*trans* isomer. But after solvent effects are taken into account, small blue shifts result, which are consistent with what is observed in the carotenoids. When "hindered" *cis* bonds exist, as in the 4-*cis* isomer, pronounced nonplanarity occurs, and the vapor phase spectrum already shows a blue shift. After the solvent effect is considered, the blue shift becomes much larger, a phenomenon also consistent with carotenoid data. The major effect on the electronic spectra introduced by the *s-cis* conformers is the relative intensity of the spectral lines. Comparing the oscillator strengths of the first transition of the conformers A of the four isomers, one sees small differences. But comparing the oscillator strengths of the same transition in the weighted spectra, one sees a marked decrease from the all *trans* isomer. Take the all *trans* and 8-*cis* isomers for example, the difference between the oscillator strengths in conformers A is 3.05–2.70 = 0.30, a 10% drop. In the weighted spectra, the difference is 2.52–1.91 = 0.61, a 25% drop. Another important change brought about by the inclusion of the *s-cis* conformers in the calculations is that the oscillator strength ratios of the first to the second transition are markedly reduced, which is again in line with experimental findings. Thus take the 8-*cis* isomer for example. The said ratio in conformer A is 2.70/0.46 = 5.9, and in the weighted spectrum, it is 1.91/1.12 = 1.7. These values are based on the calculated conformer populations at 25°C. Since lower temperatures favor the conformers with lower enthalpies more, one would expect the weighted spectra to tend toward those predicted for the A conformers at lower temperatures.

These results on the calculated electronic spectra of polyenes led us to two conclusions. One is that the solvent shift must be explicitly accounted for, and the other is that the contributions from all important *s-cis* conformers should be included. When these things are done, we see that the all *trans* polyene is calculated to show two observable absorptions, with the short wavelength one being quite weak but non-zero. The small degree of allowedness results from *s-cis* conformations. Introduction of a *cis*-alkene linkage into the middle of the chain reduces slightly the wavelength of the *trans*-peak, reduces markedly the extinction, and causes the

Table 3. Calculated absorption spectra of tetramethyl heptaenes

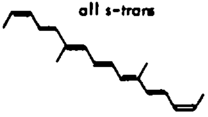
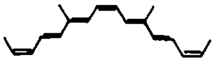
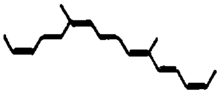
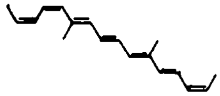
Compound	Absorption nm(f)		Solvent Shifts		λ_{max} (In solvent)		Absorption of Equil. Mixture	
	I	II	I	II	I	II	I	II
1. Heptaene–all trans								
Conformer A. Fraction 0.45 all s-trans 	362 (3.05)	256 (0)	33	0	395	256		
Conformer B. Fraction 0.41 5-s-cis	370 (2.17)	262 (0.64)	22	2	392	264		
Conformer C. Fraction 0.14 5,11 di s-cis	378 (1.82)	271 (0)	17	0	395	0		
							394 (2.52)	264(0.26)

Table 3 (*Contd*)

Compound		Absorption nm(f) I	II	Solvent Shift I	II	λnmr (In solvent) I	II	Absorption of Equil. Mixture I	II
2. Heptaene-8-cis									
Conformer A. all s-trans	Fraction 0.44	366 (2.70)	254 (0.46)	28	0	394	254		
									
Conformer B. 5 s-cis	Fraction 0.38	375 (1.57)	262 (1.55)	14	13	389	275		
Conformer C. 5,11 di s-cis	Fraction 0.18	388 (0.70)	266 (1.84)	2	17	390	284		
								392 (1.91)	274 (1.12)
3. Heptaene-6 cis									
Conformer A. all s-trans	Fraction 0.66	365 (2.80)	256 (0.32)	30	0	395	256		
									
Conformer B. 11 s-cis	Fraction 0.34	375 (1.80)	263 (1.23)	17	9	392	272		
								394 (2.46)	267 (0.63)
Heptaene-4 cis									
Conformer A. all- s-trans	Fraction 0.20	356 (2.93)	255 (0.05)	31	0	387	255		
									
Conformer B. 5, s-cis	Fraction 0.44	353 (1.99)	257 (0.77)	19	3	372	260		
Conformer C. 5, 11 di s-cis	Fraction 0.26	362 (1.61)	264 (0.06)	14	0	376	264		
Conformer D. 11 s-cis	Fraction 0.10	364 (1.95)	260 (0.86)	19	5	382	265	378 (2.08)	267 (0.63)

cis-peak to increase greatly in absorption. Introduction of a *cis*-alkene linkage nearer the end of the chain causes similar changes but to a lesser extent than when the *cis*-bond is in the center of the molecule. When a "hindered" *cis*-alkene linkage is introduced, however, the blue shifts of both transitions are calculated to be much more pronounced than when an unhindered *cis*-alkene linkage is introduced at a similar position, and some reduction in intensity is also predicted. These calculations are all in agreement with experiment. Thus the standard VESCF treatment of polyene spectra with due allowance for the factors mentioned, suffices to explain all of the observed changes in the carotenoid spectra as a function of geometry.

In conclusion it should be pointed out that many factors influence the final (composite) spectra calculated. (1) The population distribution of the various *s-cis* conformers, which in turn depends on the relative energies calculated for the conformers. (2) The dependence of the solvent shift on oscillator strength (or some other functions). (3) The parameters used in the VESCF–CI calculations. We feel that we have used in this work the best calculational methods presently available and feasible, and further improvement and/or a test for our method will only be possible from more experimental data on the electronic spectra or more conformational information on larger polyenes. It is our hope that this paper will stimulate the interest of experimental chemists to provide such data, especially on molecules containing from four to seven conjugated double bonds.

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[16] The symbol $V_{i,j}$ denotes an excited configuration resulted from an electron being promoted from molecular orbital i to molecular orbital j. Molecular orbitals 1, 2, 3. . are occupied orbitals in the ground configuration in the order of decreasing energy and −1, −2, −3. . ., unoccupied in the order of increasing energy. Thus M.O. 1 is the highest occupied and M.O. −1 the lowest unoccupied orbital.

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