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Conformational Analysis. 126. The Conformations and Electronic Spectra of Small Nonplanar Polyenes[1,2]

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Abstract: Accurate geometries for a number of small polyenes were obtained by molecular mechanics calculations. The electronic spectra of these molecules were then calculated using the standard VESCF-MO method, including doubly excited configurations in the configuration interaction treatment. Nonplanar systems can now be dealt with in a straightforward way, and the results obtained are satisfactory.

Earlier studies have shown that the variable electronegativity self-consistent field method, when both singly excited and doubly excited configurations were included in the configuration interaction treatment, was capable of giving reasonably accurate predictions of the electronic spectra of planar polyenes.[3,4] The earlier calculations were essentially limited to planar systems, because for nonplanar molecules, there was no good general method then available for determining the degree of nonplanarity, upon which the electronic spectrum is highly dependent. The molecular mechanics method now furnishes such a procedure,[5,6] and has been employed herein. The spectroscopic calculations follow the scheme and parametrization discussed earlier.[3] Depending on the particular geometric features of a given polyene it may be either planar or twisted by any amount up to 90° about one or more of the formally single bonds in the system. In the present work we have examined a number of typical molecules of varying degrees of nonplanarity. In addition, many polyenes are expected to be conformational mixtures. The molecular mechanics procedure now also gives us a method for estimating the energy differences between conformations, and hence it allows us to compute the effect of the conformational Boltzmann distribution on the expected electronic spectrum.

Of course, when a polyene has a nonplanar geometry, the σ-π separation is no longer strictly valid. It is, however, usually quite a good approximation, as shown by the agreement of calculations with experiment.

The most extensive systematic calculation of the electronic spectra of geometric isomers (including conformers) of small molecules was that by Simmons,[7] which was concerned with 1,3,5-hexatriene and 1,3,5,7-octatetraene. He had to assume "standard geometries" and planar molecules in his calculations. In addition, he neglected the effect of solvent on the transition energies. By suitable parametrization, solvent effects can be implicitly allowed for. However, a better procedure is to explicitly include solvation, which we will do here.

Results and Discussion

The exact structure of each conformer (minimum energy structure) was obtained by employing the molecular mechanics method mentioned above. A VESCF-CI treatment including all singly and doubly excited configurations[3,4] was then carried out to obtain the transition energies and oscillator strengths. The calculated spectra are summarized in Table I and compared with the available experimental data. Bond lengths and bond angles are omitted from Table I. They vary within small ranges and have relatively little effect on spectral changes. For molecules with nonplanar carbon skeletons, the dihedral angles ω of the relevant carbon-carbon bonds are given with the structural formula.[16]

A preliminary study showed several important points. First, there were always two transitions very close in energy at the longest wavelength, one strongly allowed, one forbidden, for systems with C_2 symmetry. Destroying the symmetry of the molecule led to mixing of these transitions, the oscillator strengths becoming weaker and stronger, respectively. This near degeneracy of the long wavelength $\pi \rightarrow \pi^*$ transitions has been long known with α,β-unsaturated ketones,[8] and is correctly calculated by the current method employing doubly excited configurations. Experimentally, the second transition has too low an oscillator strength to be detectable in the ultraviolet spectrum in the presence of the nearby intense band. The two transitions often show Cotton effect curves of opposite signs, however, and are readily discernible in optical rotatory dispersion or circular dichroism spectra. We find calculationally a similar near degeneracy of the long wavelength transitions with polyenes. It should be noted that calculations which do not include doubly excited configurations in the configuration interaction do not make such a prediction. The importance of including doubly excited configurations has been discussed recently.[8,9]

We found in the present work that if the bond angles and bond lengths of a polyene were kept constant, the longest wavelength $\pi \rightarrow \pi^*$ transition would vary with the dihedral angle of a single bond in the following way. The transition energy would increase to a maximum as the dihedral angle was reduced from 180° (the trans form) to 90°, then decrease with decreasing dihedral angle until $\omega = 0°$ (cis form). The oscillator strength would decrease continually with decreasing dihedral angle from 180 to 0°. The changes in transition energies and oscillator strengths were found to depend on the number of double bonds and the position in the chain of the dihedral angle being rotated.

Compounds **2–7** in Table I were dienes chosen to illustrate these findings. The transition energies and oscillator strengths of these compounds were observed to vary between wide ranges. We calculated the structures and electronic spectra of these compounds and found good agreement between the calculated and observed spectra. *trans*-Butadiene (**2**) with a dihedral angle of 180° has the highest oscillator strength, while 1,3-cyclohexadiene (**7**) of $\omega = 20°$ has the lowest oscillator strength for the first transition.

Comparison of absorption wavelengths is less direct because of the substituents on the chromophore and the solvent effect. Where vapor-phase data are lacking, the solution data have been corrected for the solvent effect by −8 nm, similar to that observed for butadiene.[10,11] Two kinds of changes in the spectra were observed when alkyl substituents were present on the chromophore. First, each of these substituents led to an increase in the absorption wavelength by approximately 5 nm (Woodward's rules).[12] Second, a cis-alkyl group led to an additional 5-nm increase.[13] The former effect was incorporated in the VESCF-CI calculation by allowing the atomic orbitals to carry a starting electronic charge commensurable with the kinds of substituents it carried.[3,4] The latter effect, however, was not accountable for with our method. Hence in Table I, 10 nm was subtracted from the observed wavelengths for compounds **3, 5, 6** and **7,** and 5 nm from compound **4** to correct for this "cis-alkyl substituent" effect. It should be noted that Fueno and Yamaguchi[13] were able to predict the cis-alkyl shift by treating the methyl group as a pseudo π orbital.

1-Bicyclohexenyl (**3**) was found to have two stable conformations; one with $\omega = 161°$ (trans) and the other with $\omega = 59°$ (cis). The trans form was calculated to be 2 kcal more stable than the cis, and would be the strongly predominant form under the conditions used to determine the UV spectrum. Hence the spectrum was calculated for the trans conformation only. 2,4-Pentadiene (**4**) was also calculated to have two stable conformers: one at $\omega = 163°$ (trans) and the other at $\omega = 52°$ (cis). The energy difference was found to be 0.32 kcal/mol, which corresponds to a population ratio of trans/cis = 0.37/0.63. Spectra for both conformers were calculated and the observed spectrum was found to lie in between. This is what would be anticipated, as the calculated absorption maxima are too close together to expect to resolve them experimentally. Compound **5** was one whose calculated absorption wavelength did not at first glance seem to agree well with the quoted observed one. Furthermore the observed extinction coefficient seemed unusually high for this molecule, which the low absorption wavelength indicates to be strongly nonplanar. However if we take the observed absorption at 179 nm as the summation of the unresolved absorptions at 198 and 171 nm, both the position and intensity of the observed transition can be explained satisfactorily. Indeed, the experimental solution spectrum shows a very broad peak. It is interesting to note that in an earlier paper[4] where we treated this molecule as planar, the calculated absorption was 35-nm longer and the oscillator strength twice as great.

When there are three or more conjugated double bonds, there exists the possibility of either the single or the double bond being in a cis conformation. In addition, more than one bond can be cis. Simmons[7] found that the lowest transition energy and the oscillator strength would decrease upon conversion of a trans to a cis bond. The effect was much more pronounced when the cis bond was a single bond. The oscillator strength depended qualitatively on the end-to-end distance of the polyene and hence was especially small for polyenes with consecutive cis bonds. Our calculations on trienes showed the same general trend. The first allowed transition of the all-trans isomer of hexatriene (**8**) lies at 240 nm with an oscillator strength of 1.19, while that of the mono s-cis isomer (**9**) lies at 252 nm with an oscillator strength of 0.68. However, the calculated difference in absorption between compound **8** and its cis isomer (**11**) is too small to be significant, although the calculations show good agreement with the experimental data.[14] It should be pointed out that *cis*-hexatriene was calculated to be planar by us, but was found to have a torsional angle of about 10° by electron diffraction measurement.[15] We believe that this indicates a planar molecule with a large torsional vibrational motion.

Compound **12,** which is significantly distorted from planarity, was calculated to absorb at a shorter wavelength than compound **11,** but not as short as butadiene (**2**), in accord with the usual ideas about conjugation and planarity. Interestingly, the change from compound **12** to compound **13,** which is disruptive of conjugation and might be expected to lead to a blue shift, actually leads to a red shift with respect to the strongly allowed transitions. However, no comparison can be made with experimental data for compounds **9, 10, 12,** and **13** because these conformations are minor components of the equilibrium. A previous calculation[6] showed that they would have much higher energies than their corresponding stable conformations, and their ultraviolet spectra are therefore not measurable. We therefore compared them with data from steroid molecules which contained similar spatial arrangements of double bonds. The observed data were corrected for the solvent effect, for the red shift caused by alkyl substituents, and for the "cis-alkyl substituent effect". The agreement is quite good.

We have discussed only the first allowed transition of the dienes and the trienes. As can be seen from our data, the next allowed transition would be in a difficultly accessible spectral region. For very long polyenes such as the carotenoids, a second absorption, the so called "cis peak", appears in the near ultraviolet region when a cis conformation is present.[17] Despite the importance of the cis peak in carotenoid chemistry, experimentally very little is known about its solvent effect, temperature dependence, steric dependence, etc. Since it is not practical to do a systematic theoretical treatment of such a large system by the present methods, and since dienes and trienes do not show a cis peak in an experimentally easily accessible region, experimental studies on the electronic spectra of tetraenes and pentaenes would be desirable.

Conclusions

Calculations on the ultraviolet spectra of polyenes abound in the literature. The present work brings out the following important points. For most planar systems which are not highly strained, standard bond lengths and angles are pretty good approximations. Except for relatively simple systems, nonplanarity is possible or likely, and the torsional angles must be approximately known if the calculated results are to apply to real molecules. With molecules which contain different conformations in equilibrium, the conformational populations must be properly taken into account.

Doubly excited configurations led to pronounced changes in the calculated spectra in general, although the strongly al-

Table I. Electronic Transitions of Small Polyenes

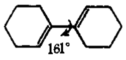
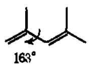
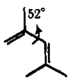
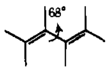
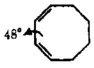
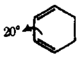
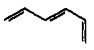
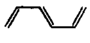
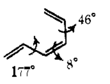
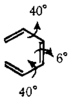
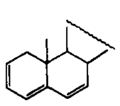
		Transition						
		Calcd			Obsd			
Compd	No.	ΔE, eV (nm)	f	ϵ^a	ΔE, eV (nm)	ε	Solvent	After solvent and "cis-alkyl" corrections
	1	7.33 (169)	0.41	12 915	7.28 (170)	17 100	Vapor[18]	
	2	5.85 (212)	0.00	0	5.92 (209)	25 200	Vapor[11]	
		5.91 (210)	0.80	25 200	5.72 (217)	21 000	Hexane[10]	
	3	5.62 (221)	0.71	22 365	5.19 (239)	19 200	Heptane[19]	
		5.57 (223)	0.00	0	5.37 (231)		Corrected^b to vapor	5.62 (221)
	4 (trans)	5.49 (226)	0.42	13 230	5.38 (231)	9 900	Cyclohexane[20]	
		5.82 (213)	0.32	10 080	5.63 (221)		Vapor[20]	5.74 (216)
	4 (cis)	5.89 (210)	0.37	11 655				
		6.35 (195)	0.03	945				
	5	6.25 (198)	0.37	11 655	No maximum between 210 and 280 nm		Ethanol[20]	
		6.60 (188)	0.07	2 200	6.63 (187)	17 600	Heptane[19]	
		7.27 (171)	0.39	12 285	6.93 (179)		Corrected^b to vapor	7.28 (169)
	6	5.87 (211)	0.42	13 230	5.44 (228)	5 800	Hexane[19]	
		6.31 (197)	0.03	945	6.71^f (185)	7 500		
		7.91 (157)	0.49	15 435	5.64 (220)		Corrected^b to vapor	5.91 (210)
	7	5.25 (236)	0.30	9 450	4.95 (251)	5 370	Vapor[21]	5.15 (241)
		5.78 (215)	0.03	945	4.84 (257)	8 000	Hexane[22]	
	8	5.04 (246)	0.00	0	5.09 (244)		Vapor[23]	
		5.17 (240)	1.19	37 485	4.87 (255)	53 000	Isooctane[24]	
		5.93 (209)	0.00	0	5.15^e (241)	18 800	Vapor[14]	
	9	4.93 (252)	0.68	21 420	4.33^c (286)	14 500	Hexane[25]	
		5.00 (248)	0.06	2 000				
		5.94 (209)	0.00	0	4.53 (274)		Corrected^b to vapor	4.70 (264)
	10	4.79 (259)	0.68	21 420	4.36^d (284)	16 200	Hexane[25]	
		4.95 (251)	0.00	0				
		5.95 (208)	0.19	5 985	4.55 (272)		Corrected^b to vapor	4.72 (262)
	11	4.99 (248)	0.00	0	4.87 (255)	41 000	Isooctane[24]	
		5.15 (241)	1.15	36 225	5.13^e (242)	15 200	Vapor[14]	
		5.95 (208)	0.00	0				

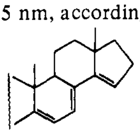
Table I (*Continued*)

		Transition						
					Obsd			
		Calcd						After solvent and "cis-alkyl"
Compd	No.	ΔE, eV (nm)	f	ϵ^a	ΔE, eV (nm)	ϵ	Solvent	corrections
	**12**	5.30 (234)	0.60	18 900				
		5.46 (227)	0.02	630				
		6.17 (201)	0.01	315				
	**13**	4.91 (253)	0.24	7 560				
		5.57 (223)	0.01	315				
		6.20 (200)	0.01	315				

^{a}Oscillator strengths were converted to extinction coefficients by fitting butadiene: $\epsilon = 31{,}500f$. Since the bandwidths and vibrational structure differ, this is only approximately correct. ^{b}Solution data for dienes were corrected to vapor phase data by −8 nm. See text. ^{c}Obtained by taking the maximum absorption wavelength of compound i and subtracting 20 nm, according to Woodward's rules. ^{d}Obtained by taking the maximum absorption wavelength of compound ii and subtracting 35 nm, according to Woodward's rules. ^{e}The first $\pi \rightarrow \pi^*$ transition of



i



ii

the trienes shows vibrational structure of three absorption peaks. We have taken the middle peaks for comparison purposes, as it is the Franck–Condon transition from the ground state in which we are interested. ^{f}The observed maximum at 185 nm is just above the cutoff point, and is probably an artifact. We interpret the experimental measurement as indicating only that the next maximum is below 185 nm with $\epsilon > 7500$.

lowed transition observed at the longest wavelength can be calculated from a simple singly excited configuration interaction treatment. Doubly excited configurations must be included in the calculations if the whole spectrum is to be well calculated. With small molecules this poses no special difficulty, but with larger molecules there is a problem with the sheer mass of numbers that must be computed in order to fill out the configuration-interaction matrix. Calculational studies on larger molecules are in progress and will be reported on later.

References and Notes

(1) For paper 125, see N. L. Allinger, D. Hindman, and H. Hönig, *J. Am. Chem. Soc.*, **99**, 3282 (1977).

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