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Transition Dipole Orientation of Linear Polyenes: Semiempirical Models and Extrapolation to the Infinite Chain Limit

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Linear conjugated polyenes have an electronic transition dipole moment for the strongly allowed $1A_g$ to $1B_u$ electronic excitation that is not oriented along the major axis of the polyene chain. In this paper, the experimental values of this off-axis angle are compared to semiempirical and ab initio theoretical predictions. The semiempirical computations are shown to be reliable and are extended to long chains ($n = 20$). The results are then extrapolated to the infinite chain limit. A nonzero value of 6°−11° for the infinite polyene is suggested by this extrapolation but state of the art ab initio results for a series of small polyenes yield a zero asymptotic value.

The spectroscopy of linear conjugated polyenes is dominated by the strongly allowed $\pi \rightarrow \pi^*$ transition from the A_g ground state to the B_u excited electronic state.[1−5] The all-trans geometry of linear polyenes has C_{2h} symmetry. In this point group an A_g to B_u excitation lies in the molecular plane but the orientation relative to the long-chain axis is not determined by symmetry. The off-axis angle (Figure 1) can have any value and still be consistent with the point group symmetry. Previous experiments have shown that this angle is on the order of 20° in condensed phase for compounds with four double bonds. From this it is expected that this angle will be about 15° for the isolated molecule. An analysis of the high-resolution rotational spectrum of *all-trans*-1,3,5,7-octatetraene touches on the issue of the transition dipole orientation but cannot distinguish between coincidence and near coincidence of the transition dipole moment with the molecular long axis.[6]

This paper concerns the ability of semiempirical methods to accurately predict the value of this off-axis angle and discusses the limit of this quantity for the case of the infinite polyene. Bond alternation in the infinite chain case is also discussed.

Background

Simple models of linear conjugated polyenes predict a range of values from 30° to almost zero for the off-axis angle of the A_g to B_u electronic transition depending on the treatment of electron correlation and the chain length. Figure 2 shows the results of Huckel molecular orbital calculations illustrating the range of possible behavior. The relevant parameter in this case is the ratio of single to double bond exchange values. In the limit where there is no exchange between ethylenic units ($\beta_S/\beta_D = 0$) the off-axis angle is 30°. This corresponds to the exciton limit in which excitation is exchanged but the electrons remain localized.[7] In the opposite limit of equal bond lengths ($\beta_S/\beta_D = 1$) the off-axis angle is small and drops rapidly toward zero as the chain length increases.

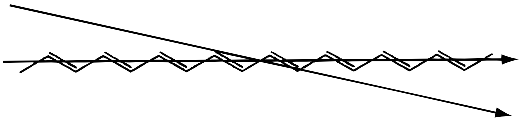

Figure 1. A linear conjugated polyene structure with an arrow illustrating the transition dipole orientation with an off-axis angle of magnitude determined by experiment and a sense indicated by theory. The long axis of the polyene is also shown.

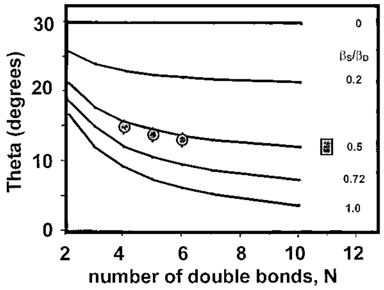

Figure 2. Variation of the off-axis angle for linear polyenes with 4, 5, 6, and 11 conjugated double bonds with chain length and comparison with results of a simple Huckel molecular orbital calculations for various of values of the ratio of the single bond to double bond exchange integral, β_S/β_D. The transition moment direction is calculated from the HOMO and LUMO coefficients. The value shown for $N = 11$ is for lycopene and is a bit higher than expected for an unsubstituted chain as discussed in the text.

The experimental determination of the angle between the long axis of the polyene chain and the transition dipole moment has been described previously.[8−11] Two methods have been used. In one method the polyene is constrained as a dilute impurity in a urea/*n*-alkane inclusion crystal.[8,10,11] The angular dependence of the fluorescence excitation spectrum of the polyene constrained in a oriented single crystal can then be used to determine the off-axis angle as defined in Figure 1. This follows from the fact that the linear conjugated polyene is aligned strictly along the *c*-axis of the hexagonal crystal. In the other entirely

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TABLE 1: Experimental and Calculated Values of the Off-Axis Transition Dipole Angle for Linear Conjugated Polyenes[a]

N	exp[8−11]	PPP VB[13]	QCFFπ PPP SDCI[14]	MNDO SDCI[15]	MNDO SCI[15]	HF CIS 6-31+G[16]	CAS SCF[17]
2			16.2			18.0	15.6
3		17.0	14.4	16.4	16.6	14.1	12.4
4	14.9	14.8	12.6	15.0	15.1	12.1	10.1
5	13.8	13.5	12.2	14.1	14.3	11.0	8.4
6	13.1		11.8	13.5	13.7	10.3	
7				13.1	13.4		
8				12.8	13.1		
9					12.9		
10					12.8		
11					12.6		
11	15[b]			14.6[c]	14.9[c]		
15					12.2		
20					11.8		

[a] The experimental values from ref 8−11 are corrected for the condensed phase dielectric effect using a cylindrical cavity model according to the procedure given in ref 12. This introduces an uncertainty of approximately 0.5° due to ambiguity in the estimation of the cavity size as discussed in refs 10 and 11. The theoretical methods used are discussed in the text and in the references cited. The value for $N = 11^*$ refers to lycopene and the MNDO calculation includes the significant effect of the methyl groups as discussed in the text. In this case the SDCI calculation was limited to the 64 lowest energy singly excited configurations and 2080 doubly excited configurations. In all cases the transition dipole angle is specified with reference to the long polyene axis which, for a symmetric polyene, bisects the terminal bonds. (See Figure 5 of ref 13.) [b] Refers to lycopene. [c] Includes methyl groups.

independent method[9] the rotational diffusion of a fluorescent polyene is determined by measurement of the time dependence of the fluorescence anisotropy in a viscous solution. The off-axis angle is determined from the magnitude of the rapid depolarization component corresponding to rotational diffusion about the long molecular axis. The experimental values for a tetraene determined in these two ways agree with each other to within 1°. The results for polyenes with 4, 5, 6, and 11 double bonds are shown in the first column of Table 1. The value for 11 double bonds is for lycopene constrained in an alkane/thiourea inclusion complex.[10] In each case the value determined for the condensed phase measurements is corrected for the anisotropic local field using the ideas developed by Myers and Birge.[12] It should be noted that these experimental methods determine the magnitude of the off-axis angle but not the absolute sense of the orientation of the transition dipole relative to the direction of the double bonds. The direction shown in Figure 1 is chosen to correspond to the theoretical determinations. It appears that all calculations agree as to this rotation sense but differ only in its magnitude.

Comparison of these experimental values with the limiting cases derived from HMO theory shows that they are intermediate between the extreme exciton ($\beta_S/\beta_D = 0$) and fully delocalized ($\beta_S/\beta_D = 1$) limits. A value of β_S/β_D of approximately 0.52 reproduces the behavior of the variation of the angle with chain length. However, as is typical with Huckel theories, a different parametrization is needed to describe the variation of the excitation energies for this same transition for the same molecules. The value of $\beta_S/\beta_D = 0.72$ gives a good fit to the excitation energies.[10] However, this parametrization clearly gives angle values that are too low.

Results

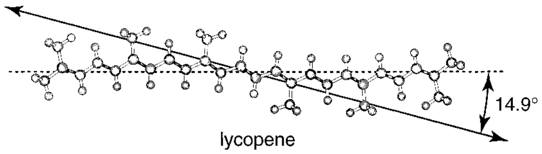

Figure 3. Structure of a model of lycopene used to compute the transition moment direction. Lycopene has terminal isoprenoid ($-CH_2-CH_2-CH{=}C(CH_3)_2$) groups in place of the trans-methyl group. Because of the lack of conjugation this is expected to have only a very minor effect.

Table 1 also shows the results of several calculations of the off-axis angle for linear conjugated polyenes using semiempirical methods and the ab initio CIS method. The first theoretical values are those of Ramashesha and Soos[13] using a Pariser−Parr−Pople π-electron theory with full treatment of π-electron correlation (complete π-electron CI). The values for 4 and 5 double bonds are in precise agreement with experiment. A similar electronic structure treatment (i.e., PPP π-electron theory) but restricted to singly and doubly excited states[14] gives results that are slightly lower than the experimental values. The next two columns give results of a MNDO full valence treatment that includes both singly and doubly excited π-electronic states or just singly excited states. In each case the parameter values from a recent reparametrization[15] were used. The single + double CI values are in quantitative agreement with experiment. The single CI values are essentially the same as the single/double CI values and can be more easily extended to longer chain lengths for purposes of extrapolation. These results, in particular the comparison with experiment, confirm the validity of this semiempirical method. Ab initio values are also given based on the Gaussian 94 HF/CIS single excitation configuration interaction[16] treatment. These values are clearly too low at this simple level of theory. Finally, CASSCF values are given. This method[17] when used with an extended ANO basis set yields excitation energies that agree with experiment to within 0.17 eV for hexatriene.

The experimental value given in Table 1 for the entry marked "11*" refers to an experiment performed for lycopene as a dilute oriented sample in a squalane/thiourea inclusion complex using polarized resonance Raman spectroscopy on a single-crystal sample. The value extracted from the experiment, after correction for the anisotropic solvent effect, is 15°. The value calculated for $N = 11$ is only 12.6°. A calculation was done that included the methyl groups that are present in lycopene. The structure used for this calculation and the resulting transition dipole moment are shown in Figure 3. The effect of the methyl groups is to tilt the transition dipole by an additional 2.3°. This makes the theoretical and experimental values coincide.

The MNDO-CI calculations (both SCI and SDCI) begin with a calculation of the ground state geometry using the MNDO-PM3 method that has proven reliable in the prediction of geometries of conjugated molecules.[18] The resulting geometry was then used for the MNDO-CI. The results of these PM3 calculations (Figure 4) are by themselves interesting and bear on the issue of the asymptotic behavior for long chains. The variation in bond lengths as a function of 1/*N* is shown in Figure 4. From bottom to top in Figure 4 are shown the bond lengths for the terminal double bonds, the central double bond for polyenes with odd numbers of double bonds, the central single bond for polyenes with even numbers of double bonds, and the end-most single bonds for all polyenes. The fact that the terminal double bonds are shorter than the inner double bonds and that the inner single bonds are shorter than the end most single bonds reflects the anticipated decrease in bond alternation toward the middle of the polyene chain. The increase in the magnitude of this positional effect with increasing chain length reflects the

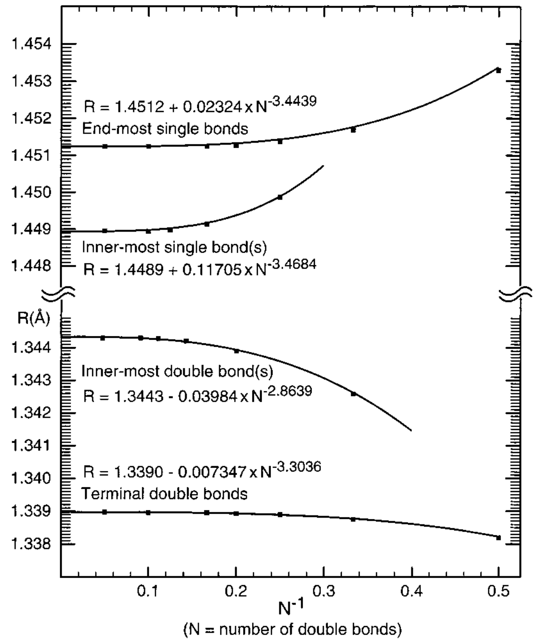

Figure 4. Variation of bond lengths deduced from PM3 calculations as a function of 1/N.

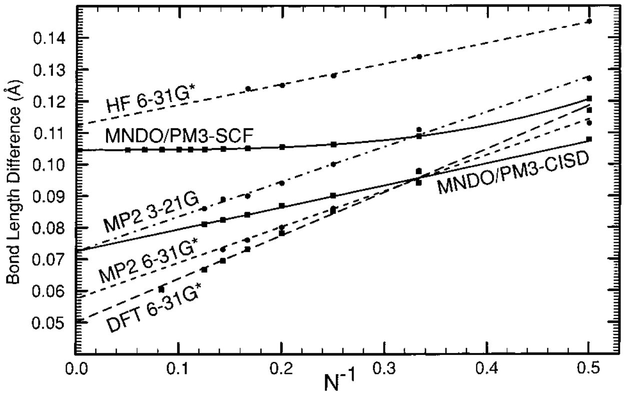

Figure 5. Variation of the difference in the bond lengths of the two most central bonds of conjugated polyenes as a function of chain length for various theoretical methods. The method used is indicated.

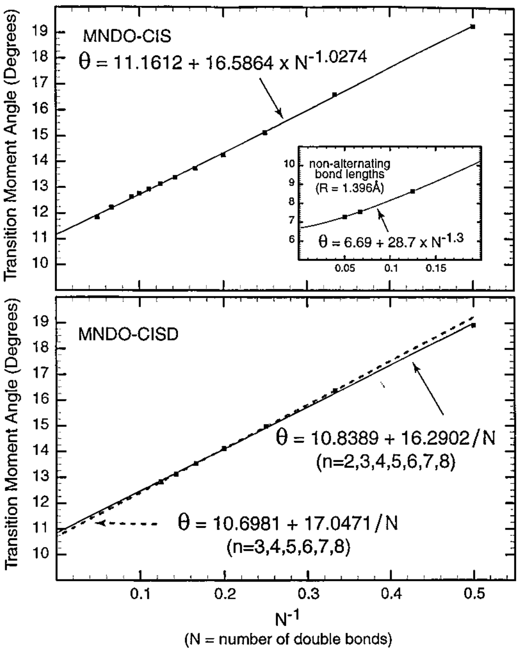

Figure 6. Variation of the off-axis angle for linear conjugated polyenes with single CI and single plus double CI MNDO calculations plotted as a function of $1/N$, where N is the number of C=C double bonds.

anticipated decrease in bond alternation with chain length. The asymptotic value of this positional effect is about twice as large (0.0053 Å) for the double bonds as for the single bonds (0.0023 Å). Of more general interest is the fact that there is clearly an asymptotic value for the bond alternation (0.1046 Å) in the middle of the polyene chain. It seems surprising that the variation in central region bond alternation and the end vs central positional effect both reach their asymptotic values so rapidly with chain length. For values of $N = 5$ and longer, the structure no longer varies with chain length.

This conclusion may, however, be dependent on the MNDO method. In order to ascertain the sensitivity of this result to method, we present in Figure 5 the difference in the bond length for the most central single and double bonds calculated with ab initio and DFT methods. The MP-2 and DFT calculations performed with the 6-31+G* basis set agree very closely with those published[19,20] and with each other and exhibit a finite slope for small $1/N$ rather than reaching a constant value. These methods, which are known to provide reliable vibrational spectra for these compounds (including the vibrational dispersion curve of polyacetylene[21]), extrapolate to a bond alternation value of about 0.05−0.06 Å for the infinite chain limit, considerably smaller than the MNDO value but still finite. A similar treatment using MNDO/PM-3 but including doubly excited configurations results in an intermediate asymptotic value.

It is clear from all of the data in Table 1 that the off-axis angle varies very slowly with chain length. Plots of the angle of the single and double CI transition moments as a function of $1/N$ are shown in Figure 6. This plot indicates that even in the limit of an infinite chain there will be a finite value to the off-axis angle. The two sets of data give very similar limiting values. A straight line through all of the SCI data extrapolates to a limiting value of 11.16°. Extrapolation of the single/double CI values yields 10.84°. It might be argued that the initial ($N = 2$) or even initial two ($N = 2$ and 3) values are expected to be anomalous and that the asymptotic behavior is expected to be reached only for longer chains. Elimination of the $N = 2$ data point from the fit for the SCI data results in an asymptotic limit of 11.02° while the SDCI limit drops from 10.84°−10.70°. Elimination of both of the first two members of the series has an even smaller effect on the extrapolated angle.

Figure 7 shows plots of the magnitudes of the axial and perpendicular components of the transition moments for the SCI and SDCI calculations again as a function of $1/N$. As N approaches infinity both of these values rise. The magnitude of the axial component is constrained to a finite value by the fact that the sum of the squares of the two components is equal to the total transition moment. Because of this the only way that the asymptotic value can go to zero is if the upward trend seen for the perpendicular component reverses and tends to zero at very long chain values. This seems unlikely.

Discussion

The major conclusion of this work is that this MNDO-CI methodology provides a reliable method for the computation of the off-axis angle of linear conjugated polyenes with a precision that is within 1°. The limiting error is probably due to the uncertainty of the condensed phase correction procedure.

From the results given above in Figures 6 and 7 we conclude that the transition dipole orientation for the infinite polyene is not parallel to the long axis of the molecule but rather makes

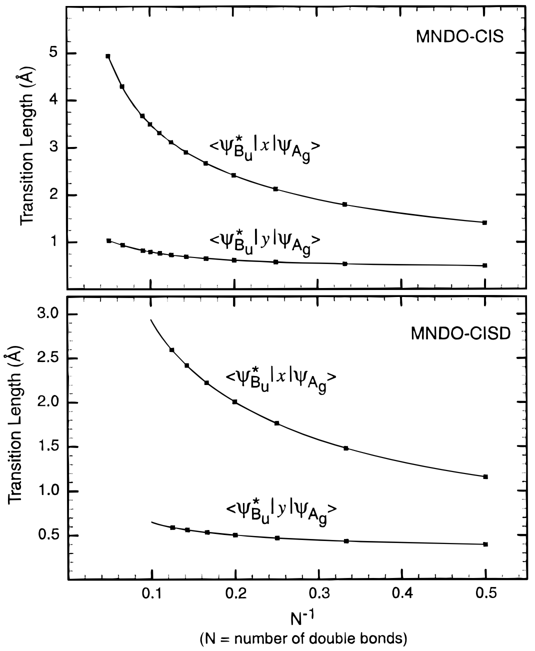

Figure 7. Variation of the axial (*x*-direction) and transverse (*y*-direction) components of the transition dipole moment for linear conjugated polyenes as calculated by the MNDO method.

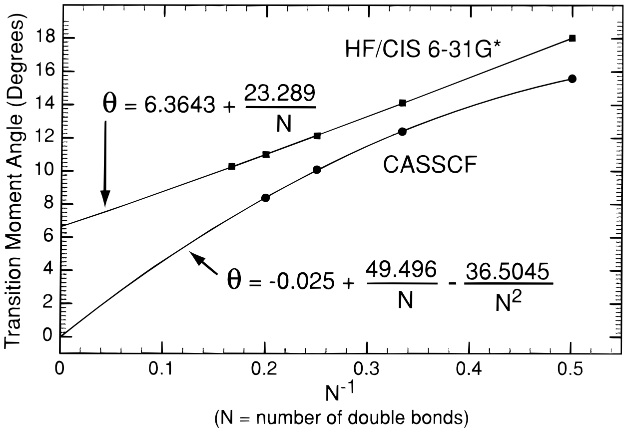

Figure 8. Transition dipole moment calculated using the HF/CIS and CASSCF methods as a function of 1/N.

an angle of about 10°−11° from the chain axis along the direction of the double bonds. This result was not anticipated by the authors.

It seems possible that the value of this finite angle might be the result of the bond alternating structure that results from the PM3 calculation. In order to test this point, calculations were performed for $N = 8$, 15, and 20 in which all of the bond lengths were set equal to 1.396 Å. The resulting plot of the off-axis angle as a function of $1/N$ is shown as an inset in Figure 6. The extrapolated limit for the off-axis angle for this extreme case is 6.7°. This value is considerably smaller than the value using the PM3 alternation results but it is clearly not zero. Another extrapolation leading to a similar conclusion is that for the HF/CIS ab initio values given in the next to the last last column of Table 1 as shown in Figure 8. These data plotted vs $1/N$ fit a straight line very precisely and extrapolate to an asymptotic value of 6.5° very close to the MNDO result without bond alternation. This HF/CIS calculation is performed with HF optimization of the geometry for each chain length. Figure 8 also shows a plot of CASSCF results. These are expected to be the most reliable set of theoretical data subject to the usual considerations concerning the effect that semiempirical methods correct for basis set deficiencies. In this case the geometries used for butadiene and hexatriene are the experimental determinations, that geometry for octatetraene is the CASSCF optimized geometry, and the geometry for decapentaene is an MP2/6-31+G* optimization. The two values that can be compared with experimental results are considerably too low. This set of data, when plotted vs $1/N$ results exhibits considerable curvature. A fit of a quadratic form to these data yields an intercept of −0.025° with a correlation coefficient of at least 0.9999. We leave it to the reader to decide which limiting behavior is most likely correct.

These results are of interest from the point of view of the interpretation of the very long chain, polyacetylene. The finite band gap observed for this material has been interpreted in terms of persistent or Peirls' instability induced bond alternation. Peirls' instability only becomes operative when the chain length reaches a point that the memory of the end effects is lost and the bond alternation vanishes. Our calculations show no evidence that this loss of end effect occurs and indicate that bond alternation persists in the infinite chain limit. This is consistent with the interpretation of infrared dichroism measurements for the CH stretch and CH wag vibrations of stretch oriented polyacetylene.[22]

The general problem of the value of the off-axis angle of the transition dipole of a finite linear polyene is of importance in applications of such molecules when used as biophysical probes.[23] This quantity is also relevant to the interpretation of structures based on dichroic spectroscopy of structues such as bacteriorhodopsin[24] that contain chromophores based on these molecular structures.

Finally, it is interesting to consider why there is an off-axis orientation for this allowed transition of linear conjugated polyenes. On symmetry grounds, there is, of course, no reason the transition should lie along the polyene molecular axis. It is only when one focuses attention on the terminal atoms that emphasis is placed on the axial nature of these structures. The opposite limit is obtained if one thinks of the linear polyene chain as a collection of (weakly) interacting ethylene units. In this case the electronic excitation can be described as a delocalized N → V ethylenic transition, i.e., a linear combination of each of the possible singly excited ethylene units. It is clear in this case that the off-axis angle will be 30° (for ideal angles). This limit is reached in the Huckel molecular orbital calculations when the exchange integral is set to zero. The real situation, which appears to be adequately described by these MINDO calculations, is intermediate between this localized limit and the fully delocalized limit obtained with the HMO treatment with equal exchange integrals.

It can be shown analytically[25] that the equal bond length HMO model results in a constant value for the perpendicular component of the transition moment. The tendency of the off-axis angle to tend to zero in the infinite chain limit implies that the on-axis component tends to infinity. While this is probably the result of such a calculation, it bears little relationship to accessible regions of reality. Disregarding experimental considerations and bond alternation, the issue of electron repulsion must be considered even within the HF/SCI approximation. It can be shown[26] that within the PPP π-electron approximation at the SCI level, the off-axis angle depends on the strength of the electron repulsion interaction, increasing with larger values. Thus, in order for the transition dipole of a polyene to lie strictly along the axis of the chain, one has to give up at least one electron repulsion) and perhaps two (bond alternation) points of contact with reality.

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