Polyene Spectroscopy. Photoelectron Spectra of the Diphenylpolyenes

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Abstract: Photoelectron spectra in the region from 6 to 20 eV have been obtained for the diphenylpolyenes stilbene, diphenylbutadiene, diphenylhexatriene, diphenyloctatetraene, diphenyldecapentaene, diphenyldodecahexaene, and diphenylhexadecaoctaene, $\mathrm{Ph}(\!=\!)_n\mathrm{Ph}$, n = 1, 2, 3, 4, 5, 6, and 8. The similarity of these spectra allows an empirical classification of the ionization peaks to be made, namely, those which are independent of chain length and those which move to lower energy as the chain length increases. The peaks which are independent of chain length are at 9.1, 11.4, and 14.2 eV and are identified as phenyl group ionizations. The peaks which change energy with chain length are identified as predominantly polyene chain ionizations from orbitals with small coefficients for the phenyl rings. The lowest energy ionizations occur at 7.94, 7.56, 7.33, 7.19, 7.05, 7.07, and about 7.2 eV for the polyenes with 1, 2, 3, 4, 5, 6, and 8 double bonds, indicating a convergence to a constant value at long chain length. This behavior is reminiscent of the convergence of the excitation energies of the dimethylpolyenes. A Hückel molecular orbital treatment of the entire series was performed, and the ionization peaks were identified with filled MO energy levels. Adjustment of the two parameters α and β_0 to fit 22 assigned transitions gave values of $|\alpha| = 6.32 \pm 0.04$ eV and $|\beta_0| = 2.80 \pm 0.04$ eV with a standard deviation between calculated and observed points of 0.07 eV which is approximately equal to the experimental error. The agreement is equally good at high and low energies.

There has been considerable recent interest in the electronic structure and spectroscopy of linear conjugated polyenes.[3-11] These compounds were among the first to be studied in terms of the relationship between color and constitution[12] and their spectroscopy had an important influence on the early development of approximate molecular quantum mechanical theories. The diphenylpolyenes have played a major role in these studies because they provide a long series of relatively stable polyenes with the same terminal group. Previous studies of the photoelectron spectra of linear polyenes have been limited to butadiene and hexatriene.[11] The principal objective of the present work is to report the observed photoelectron spectra for the series of compounds $\mathrm{Ph}(\!=\!)_n\mathrm{Ph}$ where n = 1, 2, 3, 4, 5, 6, and 8. Trends in the observed ionization energies are noted, and a classification in terms of "phenyl orbital ionizations" and "polyene orbital ionizations" is proposed.

The simplest one-electron molecular orbital picture of the ionization energies is retained throughout this work. According to this picture the observed ionization energies can be identified with one-electron orbital energies of the molecule (or molecular ion). The applicability of simple orbital pictures to polyene electronic *excitations* is described elsewhere in light of recent experimental results.[3-5,7] Our purpose in retaining this simple picture is to see to what extent it is valid in interpreting *ionization* data on a purely empirical basis. The simple Hückel molecular orbital (HMO) picture of the orbitals accurately accounts for all of the observed π ionizations between 7 and 11 eV.

Experimental Section

The diphenylpolyenes with 1, 2, 3, and 4 double bonds were obtained from commercial sources (Aldrich or Eastman). Diphenyldecapentaene was synthesized according to the method of Kuhn and Winterstein.[13] Diphenyldodecahexaene and diphenylhexadecaoctaene were obtained from Professor W. Moomaw of Williams College. The absorption spectra, melting points, and elemental analyses of these compounds showed them to be at least 99% pure. Extensive recrystallization of the tetraene and pentaene produced materials with properties identical with the starting material. The stilbene was zone refined before use. The longer compounds are easily purified because of their high melting point and low solubility. The purity of commercial diphenyloctatetraene has been discussed.[4]

Photoelectron spectra were obtained with a Perkin-Elmer Model PS-18 spectrometer using the 584 Å (21.21 eV) helium line. Full scale count rates were on the order of 10^3. The samples were inserted as solids in small capillaries and heated to 80–225°C, depending on the sample, to produce pressures of 10^{-1} to 10^{-2} Torr. The spectra were internally calibrated with the argon ionization at 15.75 eV and the xenon ionization at 12.13 eV. The accuracy of the peak positions is about ±0.05 eV due to their widths. The first ionization potentials of *cis*- and *trans*-hexatriene have been reported to be identical according to photoelectron spectroscopy,[11] and differ by less than 0.1 eV by vacuum uv spectroscopy.[6] The trans–cis isomerization which undoubtedly occurs on vaporization of the longer diphenylpolyenes will probably have negligible effects on these spectra. The vapor phase absorption spectra of the first four members of this series in the temperature range from 100 to 200°C have been previously reported.[12]

Decomposition problems occurred with diphenylhexadecaoctaene which resulted in a rising background. The temperature necessary to obtain a suitable vapor pressure was 250–260°. Internal calibration was not possible in this case so the reported ionizations in Table I are uncertain to ±0.2 eV and are probably high. The other values are ±0.05 eV based on their widths and resulting measurement errors but there may be systematic errors due to contact potential drift which increase the uncertainty to as much as ±0.1 eV. The difference between adiabatic and vertical ionization energy is ignored in this work.

Experimental Results

The photoelectron spectra of the first six members of this series are shown in Figures 1–6. All of the spectra show peaks with similar intensities at about 9.15, 11.4, and 14.2 eV. The two higher energy peaks are very broad and show a similar shape in each spectrum. A common peak at 16.8 eV is also observed. The photoelectron spectra of benzene and toluene have peaks with very similar relative intensities and shape at 9.2, 11.5, 14.2, and 16.8 eV.[14] The first peak for toluene is at 9.13 eV.[14b] The mean value for this peak for the first six members of the diphenylpolyene series is also 9.13 eV. This comparison leaves little doubt that these transitions of the diphenylpolyenes arise from orbitals which are localized on the phenyl groups.

The benzene ionization at 9.1–9.2 eV results from removal of one electron from the highest filled degenerate e_{1g} orbital.[14] The ionization at about 11.5 eV may be due to either the πa_{2u} orbital or a σ ionization. Because of the relatively great width of the diphenylpolyene ionizations at and above 11.4 eV and the probable occurrence of σ-ionizations

Table I. Observed Ionization Energies of the Diphenylpolyenes $\mathrm{Ph}\!-\!(-\!=\!-)_n\mathrm{Ph}$

n	Ionization energies (eV)					
1	7.94		9.19		10.58	11.5
2	7.56		9.09	9.99		11.4
3	7.33	8.63	9.15	9.59	10.37	11.4
4	7.19	8.38	9.12	9.98	10.80	11.4
5	7.05	8.09	9.06	9.63	10.26	11.4
6	7.07	7.94	9.17			
8	7.2 ± 0.2		9.3 ± 0.2			

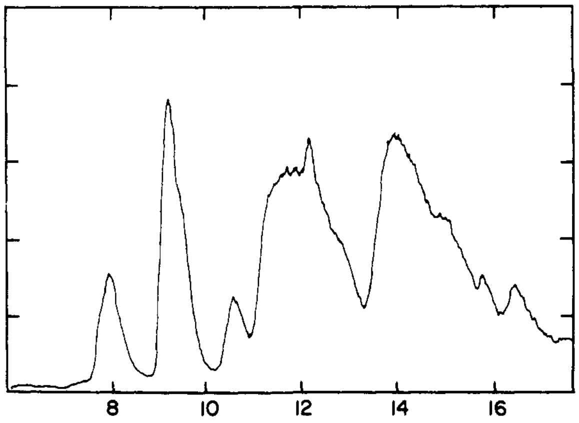

Figure 1. The photoelectron spectrum of stilbene. Sample temperature is 82°C.

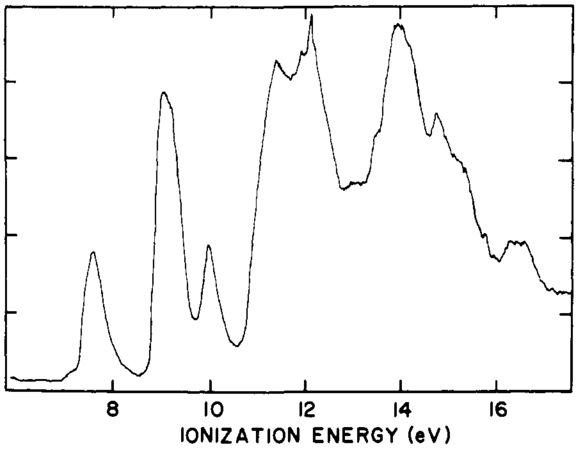

Figure 2. The photoelectron spectrum of diphenylbutadiene. Sample temperature is 105°C.

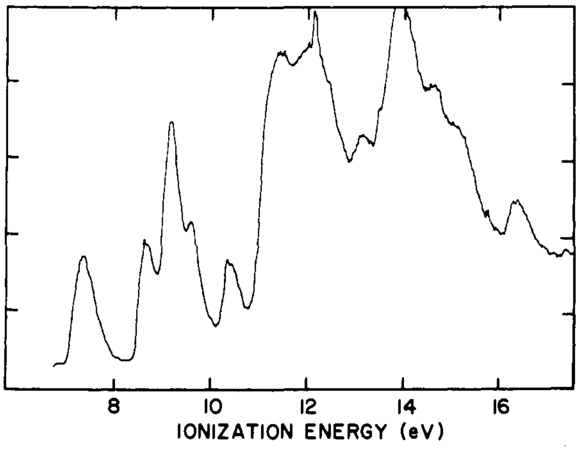

Figure 3. The photoelectron spectrum of diphenylhexatriene. Sample temperature is 140–150°C.

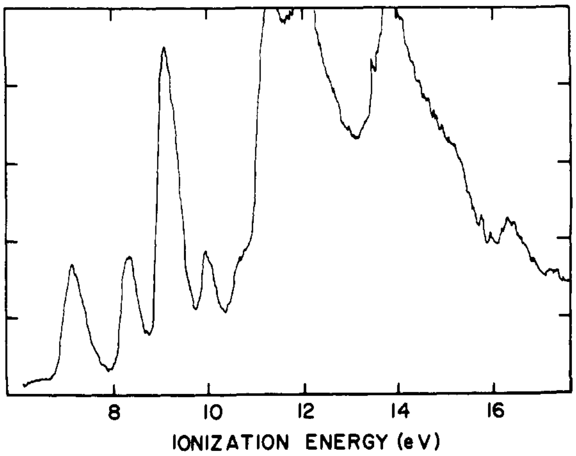

Figure 4. The photoelectron spectrum of diphenyloctatetraene. Sample temperature is 170°C.

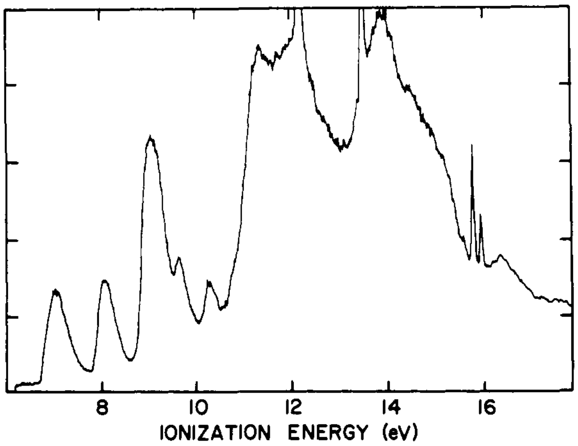

Figure 5. The photoelectron spectrum of diphenyldecapentaene. Sample temperature is 190°C.

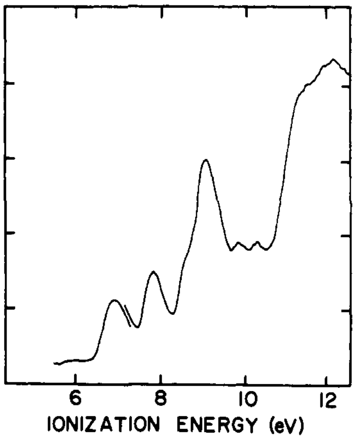

Figure 6. The photoelectron spectrum of diphenyldodecahexaene. Sample temperature is 225°C.

in this region, we restrict our attention to the region below 11 eV. The e_{1g} degenerate orbital of benzene is split by substitution. The A_2 type, π_2 orbital has a node at the point of attachment of the polyene and is unaffected by the substitution giving rise to the unshifted peak at 9.13 eV.[14] The B type, π_3 orbital is mixed with the polyene chain orbitals to an extent which depends on the polyene orbital structure and therefore the chain length. It is therefore not surprising that the photoelectron spectra of all of the diphenylpolyenes

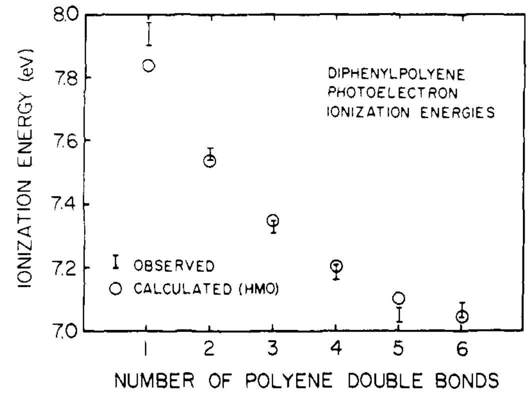

Figure 7. The lowest ionization energy of the diphenylpolyenes as a function of the number of polyene double bonds. The vertical bars, I, are the experimental points while the circles are calculated using HMO orbitals and parameters adjusted to optimize the fit to all of the data in Table I (see Figure 9 and text).

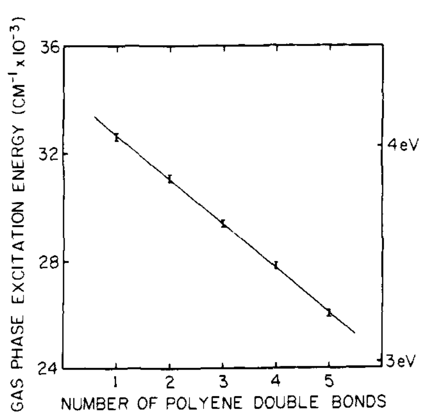

Figure 8. The excitation energies of the diphenylpolyenes corrected to gas phase values as a function of the number of polyene double bonds. The correction procedure involves the construction of a plot of $\bar{\nu}$ (cm^{-1}) vs. $\alpha_s = (n^2 - 1)/(n^2 + 2)$ for a series of solvents with refractive indices n. The linear plot is extrapolated to $\alpha_s = 0$ ($n = 1$) to obtain the gas phase value.[4] For the diphenylpolyenes with one to four double bonds the gas phase spectra have been reported.[12] The extrapolated values agree with these gas phase data to within experimental error. The extrapolated values are statistically more precise. In each case the first peak of the strongly allowed electronic transition was taken to represent the zero-zero vibronic band. The line drawn through the points is a least-squares straight line.

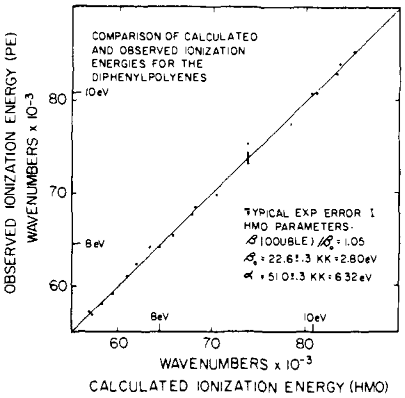

Figure 9. The correlation between observed ionization energies and those calculated from the HMO's using the given optimized parameters. The typical experimental error, ±0.05 eV, is shown.

have an invariant peak at 9.1 eV and no other constant peaks below 11 eV.

The other peaks in these spectra between 7 and 11 eV move continuously with the polyene chain length. The observed peak positions are given in Table I. The first ionization peak is of greatest interest. The observed values of 7.94, 7.56, 7.33, 7.19, 7.05, 7.07, and approximately 7.2 eV appear to converge rapidly to a constant value of 7.1 ± 0.1 eV. This behavior is shown in Figure 7. Of course, it is impossible to determine the asymptotic value of a quantity from any finite number of measurements particularly if they are subject to experimental error. It is well known that the energy of the strongly allowed excitation of the polyenes follows a similar curve, leveling off to a constant value of about 18 000 cm^{-1} (2.25 eV).[10,15-17] This has been traditionally explained by (or used as evidence for) the existence of bond length alternation in the linear polyenes with a resulting splitting of the band structure.[17,18] This bond alternation-band gap argument is based on a one-electron approximation and it therefore applies to the energies of the lower (filled) and upper (unfilled) orbitals involved in the transition. It is therefore not surprising that convergence is observed for the energy of the highest filled orbital. The actual situation is probably much more complicated, however. The basic bond alternation-band gap hypothesis has recently been examined by Ovchinnikov et al.[10] who concluded that the bond alternation expected for long polyenes can only account for 10% of the observed excitation energy gap. Experimentally, there is a contradiction between the fact that the ionization energies for the diphenylpolyenes converge to a constant value much too quickly as a function of the number of double bonds as compared to the corresponding excitation energies. In fact, when allowance is made for solvent effects by a largely empirical method,[4] the diphenylpolyene excitation energies show no sign of converging for $1 < n < 5$ (Figure 8) while the ionization energies have already converged.

Hückel Molecular Orbital Calculations

The Hückel molecular orbitals (HMO's) for the diphenylpolyenes were calculated in order to see if they correctly predict the convergence of the first ionization energy, the constant ionization at 9.15 eV, and the energies of the other π-ionizations in the 7-11 eV range. The calculations were performed using a standard program and the energies of the filled molecular orbitals were assigned to observed ionization energies. The two parameters of the theory (α and β_0) were then adjusted in a least-squares fashion to obtain the best agreement between 22 calculated and observed ionization energies. The correlation is shown in Figure 9. The standard deviation of the difference between calculated and observed ionization energies is 0.07 eV which is essentially the same as the estimated experimental uncertainty of ±0.05 eV. The degree of agreement is independent of energy. The correlation coefficient is 0.9975. The best values for the parameters are $|\alpha| = 6.32 \pm 0.04$ eV and $|\beta_0| = 2.80 \pm 0.04$ eV. These parameter values are similar to values previously obtained from electron impact appearance potential measurements ($|\alpha| = 6.2$-7.1 eV, $|\beta_0| = 2.4$-3.2 eV) but the experimental data used in these older calculations were highly uncertain and scant.[19] These values of α and β_0 are in excellent agreement with a similar correlation of HMO energies and ionization energies of aromatic molecules, ethylene, butadiene, hexatriene, and several other molecules.[20] In this case the values of $|\alpha|$ and $|\beta_0|$ obtained assuming a common β_0 for all bonds was $|\alpha| = 6.55 \pm 0.34$ eV and $|\beta_0| = 2.73 \pm 0.33$ eV and the standard deviation for 33 data points was 0.44 eV.[20] Similar but much more extensive studies result in slightly different parameter values.[21]

Figure 7 shows the calculated lowest ionization energies along with the experimental values as a function of the number of polyene double bonds. The parameters were not

Table II. Optimized HMO Fit as a Function of Bond Alternation

δ	Std dev[a]	Corr coeff	$\lvert\alpha\rvert$[b]	$\lvert\beta_0\rvert$[b]
1.00	0.075	0.9969	6.50	2.63
1.05	0.067	0.9975	6.32	2.80
1.10	0.074	0.9970	6.11	2.99
1.15	0.095	0.9950	5.88	3.20
1.20	0.128	0.9910	5.61	3.42
1.25	0.171	0.9840	5.33	3.65

[a] Standard deviation between calculated and observed points in eV using optimized values of α and β_0 for the given δ. [b] Optimized for each δ.

readjusted to fit this subclass of the data. It is seen that simple HMO theory reproduces the curvature of this plot reasonably well. The group of points in Figure 9 at about 9.1 eV (74×10^3 cm^{-1}) are the phenyl ionizations. They are calculated to occur at exactly the constant value of $\alpha + \beta = 9.12$ eV with Hückel orbital $m = 1.0000$. These orbitals are entirely localized on the phenyl rings and have a node which passes through the ring atom connected to the chain and the atom in the position para to the connection. These orbitals are doubly degenerate because of the two identical phenyl groups. The highest occupied MO is primarily localized on the polyene chain but extends significantly into the phenyl groups. For instance, for diphenyloctatetraene the sum of the squares of the HMO coefficients for the polyene atoms is 0.75.

There are two hidden variables in the HMO theory which relate to the assumed molecular geometry. Basically these variables are the ratio of the double and single bond resonance integrals β_D and β_S to the aromatic bond resonance integral β_0. These are functions of the bond lengths, but the explicit relationship to the molecular geometry need not be specified. Letting

$$\delta \equiv \beta_D/\beta_0 \text{ and } \sigma \equiv \beta_S/\beta_0 \tag{1}$$

our extra variables are δ and σ. We have assumed that $\sigma = 1/\delta$ which means that β_0 is the geometric mean of β_D and β_S. This assumes that the double bonds are shorter than the aromatic bonds and the single bonds are longer than the aromatic bonds by about the same amount. This assumption will be valid for $\delta \approx 1$. Finally, we have

$$\beta_D/\beta_S = \delta^2 \tag{2}$$

The HMO calculations were performed for various values of δ (1.00, 1.05, 1.10, 1.15, 1.20, and 1.25) and the least-squares adjustment of α and β_0 was performed for each value of δ. The standard deviation between calculated and observed values of the ionization energies, the correlation coefficients, and the optimized values of α and β_0 are given in Table II for each value of δ. It is seen that there is a weak minimum in the curve of the standard deviation vs. δ at about $\delta = 1.05$ but the standard deviation for $1.00 < \delta < 1.15$ is so close to the experimental error value of ± 0.05 eV that the significance of the minimum is questionable. The bond alternation parameter δ is not really statistically significant. Other estimates of δ are somewhat higher ($\beta_S/\beta_D = 0.72$ implies $\delta = 1.18$)[16] based on excitation energies. The bond alternation may vary with chain length and β_0 may not be the mean of β_S and β_D, but such refinements are outside the range of accuracy of our data. Inspection of Table II shows that α and β_0 are not very well determined by our data. A more realistic error range is $5.88 < |\alpha| < 6.50$ eV and $2.63 < |\beta_0| < 3.20$ eV.

Conclusions

The primary conclusion of this work is that photoelectron spectra with a considerable amount of information can be obtained for large, flexible, and relatively involatile compounds such as the diphenylpolyenes. The interpretation of the ionization energies in terms of simple π molecular orbital theory is relatively simple for this series of compounds because of the moderate number of π-ionizations at energies below the σ-ionizations and because of the occurrence of both chain length independent peaks and peaks which move uniformly with chain length. The convergence of the lowest ionization energy to a constant value at and above 5 double bonds is noted and compared with the lack of convergence of the gas phase excitation energy.

The excellent agreement which is obtained between the observed ionization energies and those calculated from simple Hückel molecular orbital theory is somewhat surprising. It is not clear what would be gained from more sophisticated calculations unless a scheme could be found which reproduces both ionization data and some other property such as the lowest excitation energies.

References and Notes

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