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The Electronic Spectrum of Diphenylhexatriyne. The Interaction of Mutually Perpendicular π and π′ Systems

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The electronic absorption spectrum of diphenylhexatriyne has been divided into two components polarized along the long and the short molecular axes by means of dichroism analysis using the stretched-polymer-film technique; *i.e.*, a reduced polarization spectrum has been obtained. This reduced polarization spectrum can be explained by a modified PPP calculation including the interaction between mutually perpendicular π and π′ systems in the conjugated system. It has been clarified that the relative intensities of the first and second bands of diphenylhexatriyne reflect the magnitude of interaction between mutually perpendicular π and π′ systems, which is quite great. The magnitude of the electron-repulsion integral between π and π′ electrons is estimated to be about 20—30 per cent of that between ordinary π (or π′) electrons.

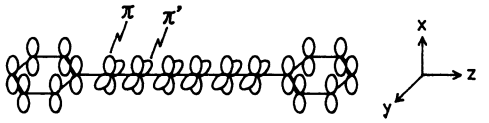
Armitage *et al.* synthesized a series of diphenylpolyynes (Ph-(C≡C)$_n$-Ph) and determined the electronic and vibrational absorption spectra.[1] They have shown that the Lewis-Calvin equation,[2] $\lambda^2=kn$, should be kept for the wavelength (λ) of the first band and the number (n) of polyynes, as in the case of polyenes, and, moreover, that the second bands increase in intensity as n increases, while the first bands become less intense. On the other hand, for the case of polyynes with terminal groups other than phenyl, Akiyama *et al.* found relationships different from the above equation between λ and n, depending on the kinds of terminal groups.[3] As has been mentioned above, studies of the electronic spectra of the polyynes have been concerned merely with phenomenological interpretations. In order to obtain more detailed information on the electronic structures and spectra of the conjugated polyynes, we measured a polarized absorption spectrum of diphenylhexatriyne using the stretched-polymer-film technique[4,5] and performed a modified PPP calculation which includes the interaction between mutually perpendicular π and π′ systems in the conjugated system including conjugated triple bonds.

Experimental

Diphenylhexatriyne was synthesized by the method described previously.[3] The polarized absorption spectrum in a stretched poly(vinyl alcohol)(PVA) film was measured in a way described elsewhere.[6] In the figure of the polarized absorption spectrum, $D_{\parallel}$ and $D_{\perp}$ denote the optical densities for the polarized-light beams, whose electric vectors are parallel to and perpendicular to the stretched direction of the PVA film respectively. The dichroic ratio (R_d) is defined as $R_d=D_{\parallel}/D_{\perp}$. R_s is the stretching ratio of the film.

Theoretical

In a PPP approximation,[7,8] each atom is considered to offer only one atomic p orbital for conjugation. It is, therefore, impossible to treat simultaneously the $\pi(2p_x)$ and $\pi'(2p_y)$ conjugated systems, which are contained, for example, in diphenylhexatriyne, by the conventional PPP method. This is because the π and π′ systems are mutually perpendicular, as is shown below, where both terminal phenyl rings are on the same plane. π means an ordinary conjugated system delocalized over the whole molecule, and π′, another conjugated system localized on the conjugated triple bonds of the hexatriyne moiety.



Thus, a modified PPP calculation which includes both π and π′ systems should be performed.[9] In this calculation, the interaction of π and π′ systems is taken into account in terms of the electron-repulsion integrals $(\pi_{2p}(r)\pi_{2p}(r)|\pi'_{2p}(s)\pi'_{2p}(s))$ between π and π′ electrons, the magnitudes of which are estimated by means of this equation;

$$(\pi_{2p}(r)\pi_{2p}(r)\,|\,\pi'_{2p}(s)\pi'_{2p}(s))=(\pi_{2p}(r)\pi_{2p}(r)\,|\,\pi'_{2p}(s)\pi'_{2p}(s))_0\times F.$$

Here, F is a parameter to be evaluated semiempirically, and $\pi_{2p}(r)$ and $\pi'_{2p}(s)$ stand for 2p atomic orbitals on the r and s atoms respectively. The values of the atomic integrals $(\pi_{2p}(r)\pi_{2p}(r)\,|\,\pi'_{2p}(s)\pi'_{2p}(s))_0$ are evaluated by assuming, after the manner of the CNDO/2 method,[15] that $(\pi_{2p}(r)\pi_{2p}(r)\,|\,\pi'_{2p}(s)\pi'_{2p}(s))_0=(\pi_{2p}(r)\pi_{2p}(r)\,|\,\pi_{2p}(s)\pi_{2p}(s))_0$. Here, the values of the atomic integrals $(\pi_{2p}(r)\pi_{2p}(r)\,|\,\pi_{2p}(s)\pi_{2p}(s))_0$ are obtained by the semiempirical method ordinarily used.[8,10] The resonance integrals between π_{2p} and π'_{2p} are all neglected, while those between 2p atomic orbitals within the π or π′ system are estimated using the variable β method.[11]

Results and Discussion

Figures 1 and 2 show the absorption spectra of diphe-

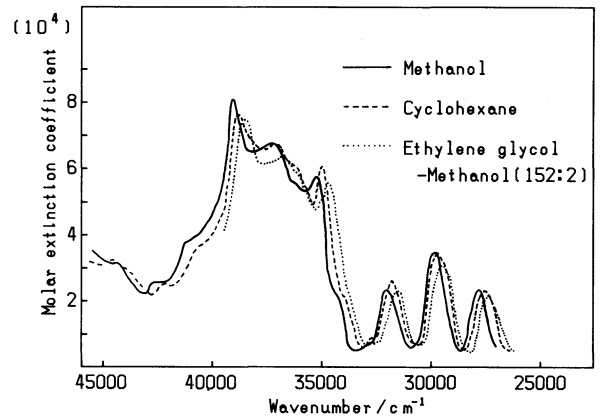


Fig. 1. Absorption spectra of diphenylhexatriyne in various solvents.

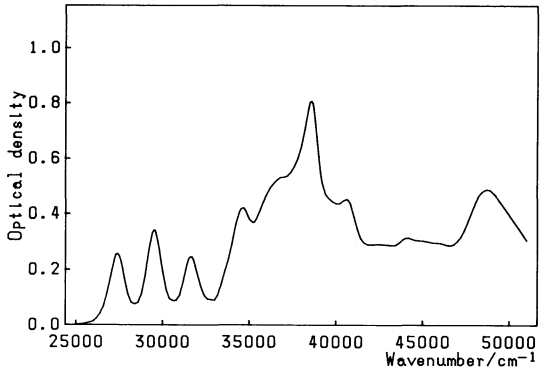


Fig. 2. Absorption spectrum of diphenylhexatriyne in the unstretched PVA film.

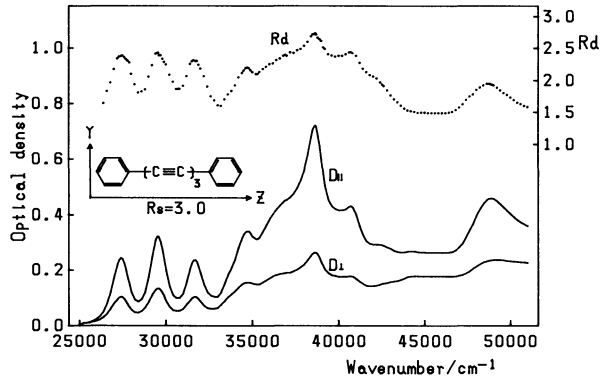


Fig. 3. The polarized absorption spectrum of diphenylhexatriyne in the stretched PVA film at room temperature.

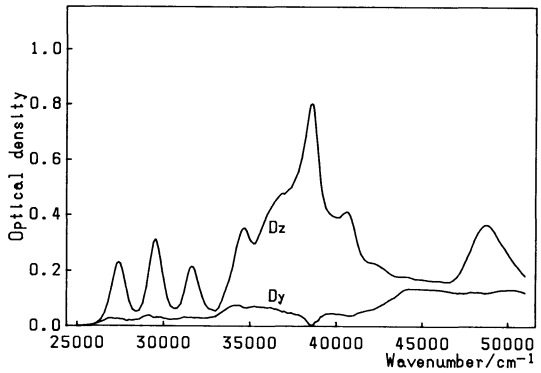


Fig. 4. The reduced polarization spectrum of diphenylhexatriyne.

nylhexatriyne in various solvents and in the unstretched PVA film respectively. The comparison of these two figures reveals that the peculiar band contour of the intense peaks in the range of 34000—41000 cm^{-1} in the PVA film is significantly different from that of the corresponding band peaks in the other solvents. This may be due to something like the Shpol'skii effect,[12,13] which is usually observed in *n*-paraffine matrices and which gives rise to very fine vibrational structures. The band peaks concerned are, therefore, considered to be members of a vibrational progression of the purely single electronic absorption band, whose 0-0 transition is at 34600 cm^{-1}. The first three peaks in the range of 27000—33000 cm^{-1} are, judging from the regularities in their shapes and positions, also considered to be members of a vibrational progression of the 27400-cm^{-1} electronic transition. These considerations are supported by the results of the modified PPP calculation discussed below; *i.e.*, there are only two allowed electronic transitions that can be assigned to the band peaks in the range of 27000—41000 cm^{-1}.

Figure 3 shows the polarized $S_n \leftarrow S_0$ absorption spectrum of diphenylhexatriyne in the stretched PVA film. In the spectrum of this compound, as has been discussed above, there are two electronic band systems whose 0-0 transitions are at 27400 and 34600 cm^{-1}. In Fig. 3, an additional electronic band is obvious at 48800 cm^{-1}. It is known that molecules adsorbed in the PVA film have a tendency that the molecular long axis inclines, on uniaxial stretching of the film, preferentially to the stretching direction of the film. Thereby, R_d values for a long-axis-polarized band are high, while those for a short-axis-polarized one are low. The R_d curve is high and takes a peak at the position of each 0-0 transition, indicating that the transitions at 27400, 34600, and 48800 cm^{-1} are polarized along the long axis (Z) of the molecule. The R_d value is highest for the most intense peak at 38600 cm^{-1}, which indicates that the intense peak at 38600 cm^{-1} may be regarded as being due purely to a longer-molecular-axis-polarized transition. Thus, taking this R_d value as a standard, the absorption spectrum of diphenylhexatriyne measured in the unstretched PVA film (Fig. 2) has been divided into two components polarized along the long (Z) and short (Y) axes by means of dichroism analysis.[4] That is, a reduced polarization spectrum has been obtained (Fig. 4). It is evident from this figure that the vibrational progressions of the two band systems, the one in the range of 27000—33000 cm^{-1}, and the other, in that of 34000—41000 cm^{-1}, and the band at 48800 cm^{-1} are all indeed polarized along the long axis of the molecule. This figure also shows that the short-axis-polarized bands are at 44000 cm^{-1} and at around 50000 cm^{-1}. Besides, a long-axis-polarized band might exist around 45000 cm^{-1}. These observations are summarized in the right column of Table 1.

In order to explain the above experimental results,

TABLE 1. COMPARISON OF THE CALCULATED AND OBSERVED RESULTS

Calc. 1				Calc. 2 F=0.0				Calc. 3 F=1.0				Calc. 4 F=0.2				Obs.			
	T.E. (cm^{-1})	f	Po.		T.E. (cm^{-1})	f	Po.		T.E. (cm^{-1})	f	Po.		T.E. (cm^{-1})	f	Po.	T.E. (cm^{-1})	f	Po.
S_1, $^1B_{1u}$	26100	2.237	Z	S_1, $^1B_{1u}$	26200	2.248	Z	S_1, $^1B_{1u}$	12300	0.057	Z	S_1, $^1B_{1u}$	25300	1.250	Z	27400	0.478	Z
⋮				⋮				⋮				⋮							
				S_4, $^1B_{1u}$	35000	1.366	Z	S_9, $^1B_{1u}$	35100	2.964	Z	S_4, $^1B_{1u}$	35100	2.589	Z	34600	1.980	Z
				⋮				⋮				⋮							
S_8, $^1B_{2u}$	43000	0.475	Y	S_8, $^1B_{2u}$	43100	0.495	Y	S_{15}, $^1B_{2u}$	43100	0.495	Y	S_8, $^1B_{2u}$	43100	0.495	Y	44000		Y
S_9, $^1B_{1u}$	43500	0.008	Z	S_9, $^1B_{1u}$	43500	0.009	Z	⋮				⋮						
⋮				⋮				S_{19}, $^1B_{1u}$	45600	0.578	Z	S_{10}, $^1B_{1u}$	43900	0.182	Z	45000		Z
S_{14}, $^1B_{1u}$	49600	0.147	Z	S_{16}, $^1B_{1u}$	49800	0.154	Z	⋮				⋮						
S_{15}, $^1B_{1u}$	50100	0.750	Z	S_{17}, $^1B_{1u}$	50400	0.840	Z	S_{27}, $^1B_{1u}$	47800	0.719	Z	S_{18}, $^1B_{1u}$	49700	0.374	Z	48800		Z
⋮				⋮				⋮				⋮						
S_{18}, $^1B_{2u}$	53200	1.262	Y	S_{22}, $^1B_{2u}$	53300	1.239	Y	S_{35}, $^1B_{2u}$	53300	1.239	Y	S_{20}, $^1B_{1u}$	50700	0.406	Z			
⋮				⋮				⋮				⋮						
												S_{22}, $^1B_{2u}$	53300	1.239	Y	50000		Y

T.E.: Transition energy. f: Oscillator strength. Po: Polarization. Y: The short axis in the molecular plane. Z: The long axis in the molecular plane.

a standard PPP calculation, in which only the π system is included, has been carried out. The calculated results can not, however, explain the above experimental results; *i.e.*, the observed 34600 cm^{-1} band can not be reproduced by this calculation (Table 1, Calc. 1). Thus, we performed a modified PPP calculation, including both π and π′ systems. The calculated results are shown in Table 1 (Calc. 2—4). The calculated transition energies and polarizations of Calc. 2, in which 0.0 is used for the value of the parameter F, well explain the observed results. However, the calculated intensity of the first-band transition is too large compared to the observation. As a result, the relative intensity of the second-band transition with respect to that of the first one can not be explained by this calculation; *i.e.*, the calculated intensity for the second transition is smaller than that for the first one, while the observed intensity for the second band is three or four times greater than that for the first one. This may be due to the fact that the interaction between π and π′ systems is neglected in Calc. 2. That is, if there is no interaction between the π system (diphenylhexatriene) and the π′ system (hexatriene), their first transitions should remain unchanged to give the first and second transitions of the united (π+π′) system (diphenylhexatriyne). If this is the case, since the conjugation of the π system is longer than that of the π′ system, and since the first transitions of both systems are polarized along the long axis, the transition energy and the transition moment for the first transition of the π system are, respectively, smaller and larger than those of the π′ system. These values are represented diagrammatically in Fig. 5 as the positions and magnitudes of the transition moment. It is, therefore, a natural result in the case of Calc. 2 that the calculated intensity for the second band of the (π+π′) system, which stems from the π′ system, is smaller than that for the first band of the (π+π′), from the π system.

However, the interaction of π and π′ systems changes the intensities (transition moments) of the first and second transitions of the (π+π′) system, as is shown in Fig. 5. In this figure, the first transition moment of the π system (diphenylhexatriene) has been made to interact with that of π′ (hexatriene) to give the combined first and second transition moments of the (π+π′) system (diphenylhexatriyne). This type of interaction between the transition moments affects only the energy levels of the excited states; the result is that the lower lying $\psi_1^0(\pi\pi^*)$ energy level is stabilized, while the upper lying $\psi_1^0(\pi'\pi'^*)$ one is destabilized. In other words, in the transition-energy scale in Fig. 5, the location of the large transition-moment vector of the π system is lowered *via* the interaction with the upper-lying, moderately large transition-moment vector of the π′ system, with their vectors being opposite in direction. As a result, the two vectors are cancelled in part, resulting in a small transition moment, *i.e.*, a weak electronic transition for the first transition of the (π+π′) system. On the other hand, the moderately large transition-moment vector of the π′ system is heightened *via* the interaction with the lower-lying large transition-moment vector of the π system, with the two vectors being the same in direction. This destabilization is small, since the transition moment concerned is also interacting with the upper-lying transition moment of π. The sum of the two vectors results, therefore, in a very large transition moment, *i.e.*, a very strong electronic transition for the second transition of the (π+π′) system.

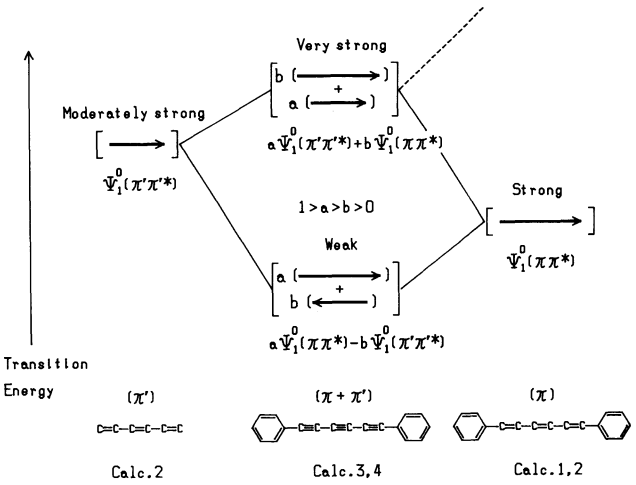
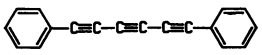
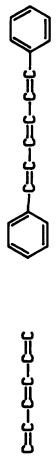


Fig. 5. The interaction of the first transition-moment vectors of the π and π′ systems, which gives the first and second transition-moment vectors of the united (π+π′) system.

TABLE 2. RESULTS OF THE CONFIGURATION ANALYSIS IN WEIGHT PER CENT



		ψ_G A_g	ψ_1 B_{1u} 27400*	ψ_2 B_{2u}	ψ_3 B_{3g}	ψ_4 B_{1u} 34600*	ψ_5 A_g	...	ψ_8 B_{2u} 44000*	ψ_9 B_{1u}	ψ_{10} B_{1u} 45000*	ψ_{11} A_u	...	ψ_{18} B_{1u} 48800*	ψ_{19} A_g	...	ψ_{22} B_{2u} 50000*
	ψ_G^0 A_g	100															
	ψ_1^0 B_{1u}		91.7			8.0											
	ψ_2^0 B_{2u}			100													
	ψ_3^0 B_{3g}				100												
	ψ_7^0 B_{2u}								100								
	ψ_8^0 B_{1u}					4.0					95.8						
	ψ_9^0 B_{1u}									100							
	ψ_{13}^0 A_g																
	ψ_{14}^0 B_{1u}												95.9				
	ψ_{15}^0 B_{1u}					1.1							2.8				
	ψ_{16}^0 B_{3g}																
	ψ_{17}^0 B_{2u}																100
	ψ_{18}^0 A_g													30.4			
	ψ_1^0 B_{1u}		7.9			86.1					3.7						
	ψ_2^0 A_g																
	ψ_3^0 A_g						3.2							42.9			

ψ_i: The total wavefunction of diphenylhexatriyne. ψ_i^0: The total wavefunction of the reference molecule.
*: The observed transition energy in wave number.

Thus, the relative intensities of the first and second bands of diphenylhexatriyne reflect the magnitude of the interaction between the π and π' systems. That is, the fact that the intensity of the second-band system is larger than that of the first-band system implies that there is a considerable interaction between the π and π' systems. The magnitude of the interaction between the two π systems is controlled by the magnitude of the parameter F used in the equation to obtain the electron-repulsion integral between π and π' electrons, and it is manifested by the mixing coefficients a and b given in Fig. 5. For zero interaction (F=0.0), a=1 and b=0. For non-zero interaction (F>0.0), the relation $1>a>b>0$ holds ($a^2+b^2=1$).

The calculated results for a large interaction (Calc. 3, F=1.0) deviate greatly from the observed results as to the location and intensity of the first transition. That is, the first transition moment of diphenylhexatriyne is stabilized too much and cancelled to an excessive degree. The appropriate value of the parameter F is 0.2—0.3 (Calc. 4), which yields reasonable intensities for the first and second transitions. The evaluation of the parameter F has already been discussed elsewhere.[9] In the CNDO/2 method, F is regarded as 1.0.[15] The results of Calc. 4 reproduce the observed spectrum fairly well. That is, the long-axis (Z) polarized bands observed at 27400, 34600, 45000, and 48800 cm^{-1} correspond to the calculated transitions ($^1B_{1u}\leftarrow{}^1A_g$, D_{2h}) from S_0 to S_1, S_4, S_{10}, and S_{18} respectively, while the short-axis (Y) polarized bands at 44000 and 50000 cm^{-1} correspond to the transitions ($^1B_{2u}\leftarrow{}^1A_g$) to S_8 and S_{22} respectively.

Incidentally, the interaction scheme given in Fig. 5 also gives an explanation of the finding made by Armitage *et al.* that, in a series of diphenylpolyynes (Ph-(C≡C)$_n$-Ph), the second bands increase in intensity as n increases, while the first bands become less intense. As n increases, the magnitudes of the transition moments of both the π and π' systems become larger, which results in a larger value (an increase in intensity) for the plus combination (the second bands) of the two vectors, but their difference may, though not easy to predict *a priori*, become smaller, which results in a smaller value (a decrease in intensity) for the minus combination (the first bands). F and the mixing coefficients (a and b) are now assumed to be constant, irrespective of n.

In order to ascertain the nature of each electronic transition of diphenylhexatriyne, configuration analysis[14] has been performed for the wavefunctions of Calc. 4 whose results are in good agreement with the observations as has been discussed above; some interesting results have thus been obtained (see Table 2). The main contributors to the S_1 and S_4 states are, respectively, the π-π^* and π'-π'^* configurations; *i.e.*, the $S_1\leftarrow S_0$ observed at 27400 cm^{-1} is regarded as a typical π-π^* transition, and the $S_4\leftarrow S_0$ at 34600 cm^{-1}, as a π'-π'^* within the π' framework perpendicular to the π system. The eighth excited state (S_8) corresponding to the short-axis polarized 44000 cm^{-1} band consists of the π-π^* configuration ($\psi_{7th}^0(\pi\pi^*)$=100%), in which the electronic transition occurs from the MO delocalized over the π system to the MO localized on the two phenyl rings, or *vice versa*.

It should, moreover, be noted that a mixing between mutually perpendicular π and π' electron systems results from a considerable degree of configuration interaction. That is, the S_1 ($\psi_{1st}^0(\pi\pi^*)\simeq$92%) state con-

tains about 8% of the π'–π'^* character ($\psi^0_{1st}(\pi'\pi'^*) \simeq 8\%$), and the S_4 ($\psi^0_{1st}(\pi'\pi'^*) \simeq 86\%$) state, about 12% of the π–π^* character ($\psi^0_{1st}(\pi\pi^*) \simeq 8\%$, $\psi^0_{5th}(\pi\pi^*) \simeq 4\%$).

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