CHEMISTRY LETTERS, pp. 357-360, 1977. Published by the Chemical Society of Japan

POLARIZED TRIPLET-TRIPLET ABSORPTION SPECTRUM USING STRETCHED POLYMER FILM AT LIQUID NITROGEN TEMPERATURE: DIPHENYLACETYLENE

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Measurements of a polarized triplet-triplet absorption spectrum using stretched polymer films have been attempted at liquid nitrogen temperature. The polarizations of the triplet-triplet transitions of diphenylacetylene were determined, and the molecular structure in the excited triplet state was discussed.

In a previous paper,$^{1)}$ we described a procedure to determine a polarized triplet-triplet ($T_n \leftarrow T_1$) absorption spectrum with the aid of the stretched polymer film technique at room temperature, and applied this method to determine the polarizations of the $T_n \leftarrow T_1$ transitions of phenanthrene. In this investigation, we attempted to measure the polarized $T_n \leftarrow T_1$ absorption spectrum at 77 K, and determined the polarizations of the $T_n \leftarrow T_1$ bands of diphenylacetylene.

The commercially available diphenylacetylene (Tokyo Kasei Co. Ltd.) was purified by repeated recrystallizations from ethanol. The polarized $T_n \leftarrow T_1$ absorption spectrum at liquid nitrogen temperature was measured with a modified Ushio UPF-101 flash spectrophotometer, and the optical arrangement has been shown in Fig. 1.

Figure 2 shows the polarized $T_n \leftarrow T_1$ absorption spectrum of diphenylacetylene in the stretched polymer (polyvinylalcohol) film at liquid nitrogen temperature,

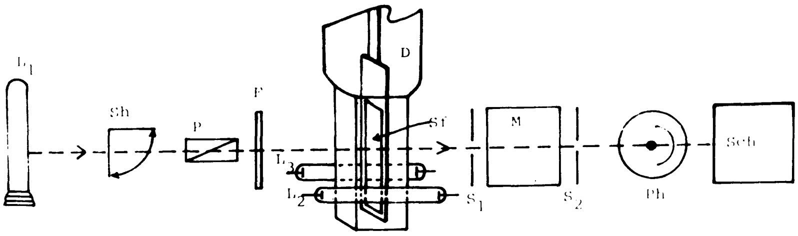


Fig. 1. The optical arrangement for the measurement of the polarized $T_n \leftarrow T_1$ absorption spectrum.
L_1: 150 W Xe-lamp, L_2 and L_3: Xe-flash lamp,
Sh: shutter, P: polarizer, F: filter, Sf: sample film, D: Dewar's vessel, S_1 and S_2: slit, M: monochrometer, Ph: photomultiplier, Sch: synchroscope

in which the polarized $S_n \leftarrow S_0$ spectrum at the same temperature is also shown for comparison. In this figure, $D_{\parallel}$ and $D_{\perp}$ are absorbances measured for incident light polarized respectively parallel to and perpendicular to the stretched direction of the polymer film, Rd is a ratio of the absorbances, Rd = $D_{\parallel}/D_{\perp}$, and Rs is a degree of stretching of the film.

The $S_n \leftarrow S_0$ spectrum of diphenylacetylene in the near ultraviolet region consists of two electronic bands, whose 0-0 transitions are at 33.18 and 44.25 kK.[2)] The polarized $S_n \leftarrow S_0$ spectrum shows that the 33.18 kK band is polarized along the longer molecular-axis, because the Rd values for the 33.18 kK band are large compared with those in the tail of the 44.25 kK band. These results are in good agreement with the already published data, and the two bands at 33.18 and 44.25 kK can be safely assigned to $^1B_{1u} \leftarrow {}^1A_g$ and $^1B_{2u} \leftarrow {}^1A_g$ transitions, respectively.

The $T_n \leftarrow T_1$ absorption spectrum of diphenylacetylene has already been measured in various solvents at room temperature.[3)] For instance, this compound shows a relatively strong $T_n \leftarrow T_1$ band in the wavenumber region 22.5-28.5 kK, whose band maximum is at 23.90 kK in glycerol. The corresponding band is observed at 23.85 kK in the polymer film at 77 K, besides a very weak band is observed in the longer wavelength side (18-23 kK) of the 23.85 kK band. The Rd values for the 23.85 kK band are relatively large and these values are almost the same with those of the 33.18 kK $S_n \leftarrow S_0$ band, indicating that the strong 23.85 kK $T_n \leftarrow T_1$ band is polarized along the longer molecular-axis. To know a more detailed nature of these $T_n \leftarrow T_1$

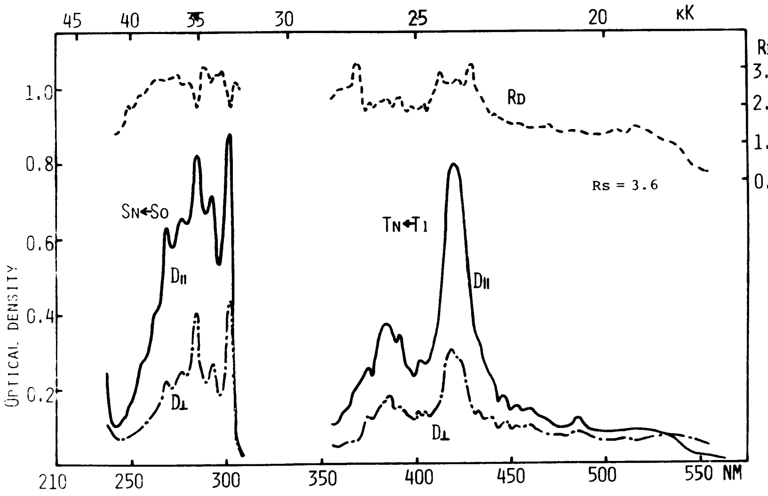
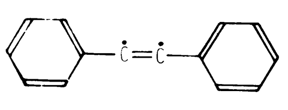


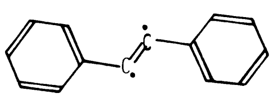
Fig. 2. Polarized $T_n \leftarrow T_1$ and $S_n \leftarrow S_0$ absorption spectra of diphenylacetylene in the stretched polymer film at 77 K.

bands, we carried out MO calculations for this molecule. In the MO calculations, a modified PPP method developed by Nishimoto and Forster$^{4)}$ is adopted, i.e., the valence state ionization potential and electron affinity for the carbon atom are taken to be 11.22 eV and 0.62 eV, respectively, and the resonance integrals among the adjacent carbon atoms are adjusted at every iteration of the SCF calculations by the equation, $\beta_{CC} = -0.51p_{CC}-1.84$ eV. Here, p_{CC} is the π-bond order. The transition moments from the lowest triplet state to the higher triplet states are calculated by the method described by Pariser.$^{5)}$

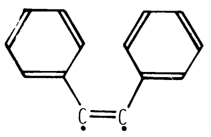
As for the molecular structure of diphenylacetylene in the excited triplet



D_{2h}



C_{2h}(trans)



C_{2v}(cis)

Table 1. Comparison of the calculated and observed transition energies, intensities and polarizations for the $T_n \leftarrow T_1$ transitions of diphenylacetylene

	Transition energy(eV) (Calc.)			Oscillator strength (Calc.)			Polarization*			(Obs.)		
	D_{2h}	C_{2h}	C_{2v}	D_{2h}	C_{2h}	C_{2v}	D_{2h}	C_{2h}	C_{2v}	Transition energy(eV)	Intensity	Polarization
T_2	1.53(^3A_g)	1.05(^3A_g)	1.07($^3A_1$)									
T_3	1.88($^3B_{1u}$)	1.52(^3B_u)	1.52($^3B_2$)			0.0124			90°			
T_4	2.17($^3B_{3g}$)	1.71(^3A_g)	1.71($^3A_1$)			1.0668			0°			
T_5	2.17($^3B_{2u}$)	1.72(^3B_u)	1.73($^3B_2$)									
T_6	2.32(^3A_g)	1.84(^3A_g)	1.86($^3A_1$)									
T_7	2.37($^3B_{1u}$)	1.95(^3B_u)	1.96($^3B_2$)									
T_8	2.88($^3B_{2u}$)	2.44(^3B_u)	2.40($^3A_1$)									
T_9	2.89($^3B_{3g}$)	2.44(^3A_g)	2.43($^3B_2$)	0.0634	0.0391	0.0005	90°	31.2°*1	0°	2.48	weak	short-axis
T_{10}	3.90(^3A_g)	3.55(^3A_g)	3.28($^3A_1$)	2.2062	1.6685	0.0655	0°	-51.0°*2	90°	2.96	strong	long-axis
T_{11}	4.43($^3B_{3g}$)	4.03(^3A_g)	3.75($^3B_2$)			1.5981			90°			
	$T_1={}^3B_{1u}$	$T_1={}^3B_u$	$T_1={}^3B_2$									

*With respect to the $C\equiv C$ bond axis, *1 Approximately along the shorter molecular-axis, *2 Approximately along the longer molecular-axis

state, three different structures may be considered. Therefore,we carried out the MO calculation for each molecular structure, and the results are compared with the experimental ones in Table 1. From this table, we may conclude that diphenylacetylene takes trans form in the excited triplet state. If this is the case, the strong and weak $T_n \leftarrow T_1$ bands at 23.85 kK and around 20 kK can be assigned to $^3A_g \leftarrow {}^3B_u$ transitions. The former band is polarized approximately along the longer molecular-axis, and the latter one approximately along the shorter molecular-axis.

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(Received January 11, 1977)