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# $\pi$–$\pi^*$ and $\pi'$–$\pi'^*$ Electronic Transitions of Diphenylbutadiyne

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**Abstract:** The polarized absorption spectrum of diphenylbutadiyne has been measured in the stretched polyethylene film, and the polarizations of electronic and vibrational bands are determined. It has been clarified that, for instance, the 30 250- and 38 020-cm$^{-1}$ electronic bands are polarized along the longer molecular axis and the 30 250-cm$^{-1}$ band is assigned to an ordinary $\pi$–$\pi^*(S_1 \leftarrow S_0)$ transition and the 38 020-cm$^{-1}$ band to a $\pi'$–$\pi'^*(S_6 \leftarrow S_0)$ transition. Here, the $\pi'$ electronic system is perpendicular to the ordinary $\pi$ system. The $\pi$–$\pi^*$ bands of diphenylbutadiyne show a weak Shpol'skii effect in the polyethylene matrix. The $\pi'$–$\pi'^*$ band behaves as opposed to the Shpol'skii effect, i.e., the intensity of the $\pi'$–$\pi'^*$ band is lowered with lowering temperature. From a guest–host interaction model and an MO calculation, it is suggested that the effect of the guest–host coupling is mainly manifest in the $\pi'$–$\pi'^*$ band, and the band is, therefore, considered as having mainly a so-called phonon band character and each $\pi$–$\pi^*$ band a non-phonon band character. In some other diphenylpolyynes, the $\pi'$–$\pi'^*$ transitions have also been found.

## I. Introduction

Despite a pronounced delocalization of the $\pi$ electrons over the benzene and acetylene moieties in phenylacetylene, the 279-nm $^1L_b(^1B_2) \leftarrow {}^1A(^1A_1)$ one-photon band of this compound is predicted to be very weak. The largely forbidden character of this band appears to arise from cancellation of $^1B_b$ terms, which are the principal source of the $^1L_b$ band intensity of a substituted benzene,[1,2] due to the two types of intramolecular charge-transfer (CT) configurations (acetylene → benzene* and benzene → acetylene*).[3] In fact, both transition densities due to these two CT transitions are localized on the benzene fragment and have the same short-axis-polarized $^1B_b$ character with their transition moment vectors being opposite in direction, which results in the cancellation of the two vectors. In diphenylhexatriyne, the CT transitions mentioned above are allowed and observed as the third band.[4] Again in this case, the transition densities constitute the short-axis-polarized $^1B_b$ terms localized on the two terminal benzene fragments with their moment vectors being the same in direction. In contrast to the case of phenylacetylene, however, the transition moment vectors due to the two CT transitions, which are both short-axis-polarized, are the same in direction and are not cancelled as will be exemplified in details for diphenylbutadiyne in this paper. On the other hand, the $^1L_a$ band of phenylacetylene in the higher energy region is fairly strong ($\epsilon \simeq 17\,000$). This is due to the transition moment vectors of the $^1L_a$ transition of the benzene moiety and the transition of the acetylene moiety, both of which are polarized along the long axis and are colinear with their directions being the same. Therefore, the elongation of the conjugation of phenylacetylene through incooperating additional benzene and acetylene moieties as in diphenylpolyyne ($C_6H_5$—$(C{\equiv}C)_n$—$C_6H_5$) results in a red shift of this $^1L_a$ band, making this band observed as the first band for diphenylpolyyne as will be proven for diphenylbutadiyne in this work.

In the case of diphenylpolyyne, there is another aspect of spectroscopic behavior different from phenylacetylene. In both molecules, there are two kinds of $\pi$ electronic systems, $\pi$ and $\pi'$, which are mutually perpendicular ($\pi$ means the ordinary conjugated system delocalized over the whole molecule and $\pi'$ another conjugated system localized on polyyne or the acetylene fragment). The $^1L_b$ and $^1L_a$ bands mentioned above are all originated from the $\pi$ system ($\pi$–$\pi^*$ bands). The difference is concerned with the band originated from the $\pi'$ system ($\pi'$–$\pi'^*$ band). In the UV region, the $\pi'$–$\pi'^*$ band is observed for diphenylpolyyne but not for phenylacetylene. This is, of course, due to the conjugation in $\pi'$ being long enough for the former but too short for the latter. For diphenylhexatriyne, we indeed clarified that the second band positioned between the $^1L_a$ and $^1L_b$ bands is assigned as the $\pi'$–$\pi'^*$ band, and its high intensity is evidence for the significantly greater interaction between $\pi$ and $\pi'$ electronic systems.[4]

In the previous investigation,[4] we have also pointed out some possibility of the Shpol'skii effect[5,6] for diphenylhexatriyne in the poly(vinyl alcohol) (PVA) film. This effect is usually observed in *n*-alkane matrices. That is, when an appropriate aromatic guest molecule is introduced in frozen *n*-alkane host matrices, quasiline spectra emerge on a diffuse background. The quasilines are

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[†] Aoyama Gakuin University.

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(1) Albrecht, A. C. *J. Chem. Phys.* **1960**, *33*, 156.

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**Table I.** Comparison of the Observed and Calculated Results for Diphenylbutadiyne

| | | transtn energy $cm^{-1}$ | | intensity | | polarization | | |
|---|---|---|---|---|---|---|---|---|
| | | calcd | obsd | calcd ($f$)[a] | obsd ($f$) | calcd | obsd | notes |
| $S_1$ | ($^1B_{1u}$) | 27 720 | 30 250 | 1.3315 | 0.598 | Z[b] | Z | $\pi$–$\pi^*$ |
| $S_2$ | ($^1B_{2u}$)[d] | 33 479 | | forb | | | | |
| $S_3$ | ($^1B_{3g}$) | 33 484 | | forb[e] | | | | |
| $S_4$ | ($^1A_g$) | 38 986 | | forb | | | | |
| $S_5$ | ($^1A_g$) | 39 341 | | forb | | | | |
| $S_6$ | ($^1B_{1u}$) | 41 649 | 38 020 | 1.2247 | 0.551 | Z | Z | $\pi'$–$\pi'^*$ |
| $S_7$ | ($^1B_{3g}$) | 43 384 | | forb | | | | |
| $S_8$ | ($^1B_{2u}$) | 43 544 | 43 460 | 0.5436 | | Y[c] | Y | $\pi$–$\pi^*$ |
| $S_9$ | ($^1B_{1u}$) | 46 139 | 44 110 | 0.8920 | | Z | Z | $\pi$–$\pi^*$ |
| $S_{10}$ | ($^1A_g$) | 46 260 | | 0.0000 | | Y | | $\pi$–$\pi^*$ |
| $S_{11}$ | ($^1A_g$) | 48 378 | | forb | | | | |
| $S_{12}$ | ($^1B_{2u}$)[d] | 48 476 | | forb | | | | |
| $S_{13}$ | ($^1B_{3g}$) | 48 487 | | forb | | | | |
| $S_{14}$ | ($^1A_u$) | 50 039 | | forb | | | | $\pi$–$\pi'^*$ |
| $S_{15}$ | ($^1A_u$) | 50 039 | | forb | | | | $\pi'$–$\pi^*$ |
| $S_{16}$ | ($^1A_g$) | 52 521 | | forb | | | | |
| $S_{17}$ | ($^1B_{1u}$) | 53 005 | 49 500[f] | 0.5874 | | Z | Z | $\pi$–$\pi^*$ |
| $S_{18}$ | ($^1A_g$) | 53 120 | | forb | | | | |

[a] Oscillator strength. [b] The long molecular axis. [c] The short molecular axis. [d] These transitions are allowed to group theoretically, but they are forbidden by Pariser's Parity rule. [f] Measured in the stretched PVA film at room temperature.

associated with non-phonon lines and the diffused background with a phonon band.[7] From the temperature dependences of the quasiline intensity, position, and width, it is indeed shown that non-phonon lines are indicative of the weakness of the guest–host coupling.[8] The quasiline spectra are, therefore, attributed to isolated molecules. Recently, it is, however, claimed from the observed hypochromic or hyperchromic effect in quasiline spectra that some host molecules responsible for quasiline spectra experience intermolecular guest–guest interaction and, consequently, cannot be considered as strictly isolated even at low guest concentration.[9]

In the present investigation, the nature of $\pi$–$\pi^*$ and $\pi'$–$\pi'^*$ transitions of diphenylbutadiyne, being considered to be a homologue of the previously studied diphenylhexatriyne, is clarified from the results of the polarized UV absorption spectrum, solvent effects, and temperature dependences of the absorption spectrum and MO calculations. In connection with temperature dependences of the absorption spectrum, some new aspects of the Shpol'skii effect, which are peculiar to the molecules having the mutually perpendicular $\pi$ and $\pi'$ electronic systems, will be pointed out. Furthermore, MO calculations are systematically performed to reproduce the observed changes in transition energies and intensities of the first and the second electronic bands of diphenylpolyyne ($C_6H_5$—($C{\equiv}C$)$_n$—$C_6H_5$) for the variation of $n$.[10]

## II. Experimental Section

The commercially available diphenylbutadiyne (Aldrich Chemical Co, Ltd.) was used without further purification. The polyethylene film used for the measurement of the polarized absorption spectrum was obtained commercially (Okura Kogyo Co., Ltd.), and the film was washed with cyclohexane to remove impurities. The polarized absorption spectrum was recorded on a Shimadzu UV-360 type automatic recording spectrophotometer attached with a rochon type polarizer and a cryostat.[11]

## III. Results and Discussion

**Assignment and Analysis of the Electronic Transitions.** The UV absorption spectrum of diphenylbutadiyne is not influenced greatly by changes in the solvent polarity, as shown in Figure 1. The 0–0 transitions of the first and second electronic bands are at 30 510 and 38 430 $cm^{-1}$ in cyclohexane, respectively, and both transitions accompany fine structures. In order to know the polarization of each band, the polarized $S_n \leftarrow S_0$ absorption spectrum has been measured in the stretched polyethylene film at 97 K, and the result is shown in Figure 2. In this figure, $D_\parallel$ and $D_\perp$ are optical densities measured with polarized light beams whose electric vectors are parallel to and perpendicular to the stretched direction of the polymer film, respectively. Rd is a ratio of $D_\parallel$ and $D_\perp$ (Rd = $D_\parallel/D_\perp$). In the polymer film, the 0–0 transitions of the first and second electronic bands have been observed at 30 250 and 38 020 $cm^{-1}$. It is clear that both 0–0 transitions are polarized along the longer molecular axis, since the Rd curve shows maxima at the two 0–0 band positions. These results are in agreement with those of Tanaka et al. obtained from

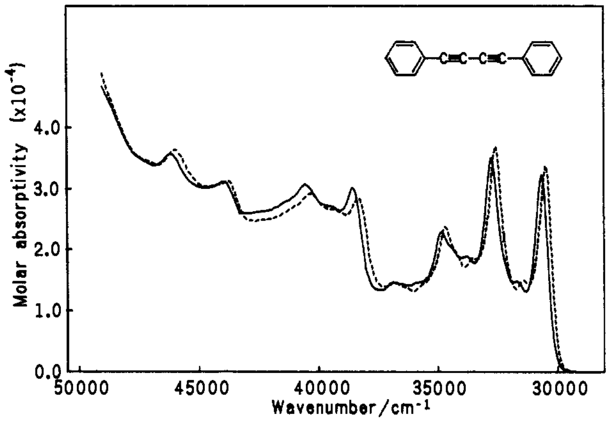

**Figure 1.** The absorption spectra of diphenylbutadiyne in ethanol (—) and cyclohexane (---).

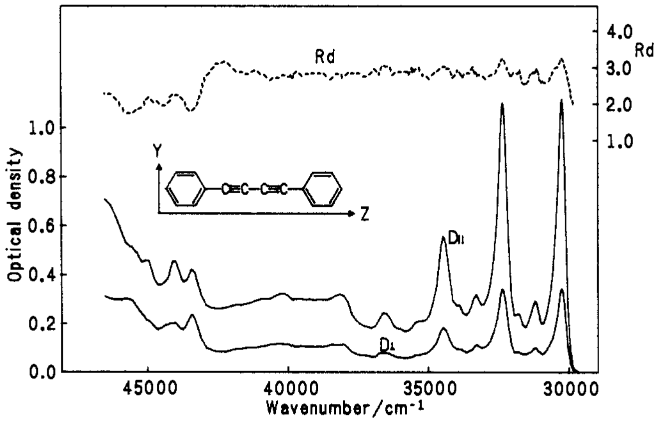

**Figure 2.** The polarized absorption spectrum of diphenylbutadiyne in the stretched polyethylene film at 97 K.

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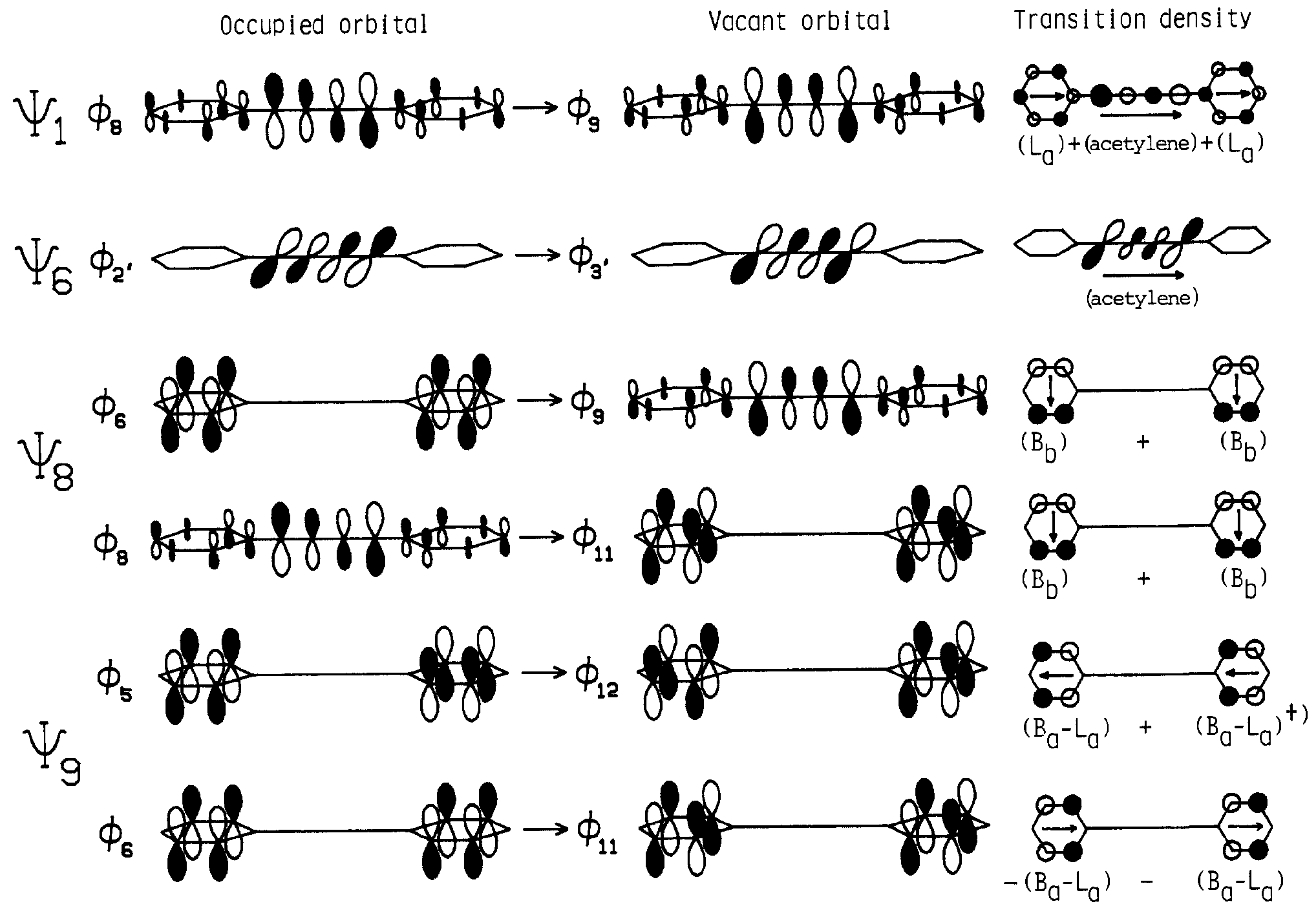
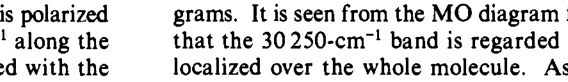


**Figure 3.** Diagrammatic representations for the MO's and transition densities concerning the main contributors for the electronic transitions of diphenylbutadiyne. This is diagrammatically explained as



the polarized absorption spectrum by using the single crystal technique.[12] The spectrum in the crystalline state obtained by them is very diffuse, and the spectrum in the wavelength region higher than 41 700 cm$^{-1}$ is not obtained. Diphenylbutadiyne shows two more electronic bands at 43 460 and 44 110 cm$^{-1}$. Rd curve shows a minimum around 43 460 cm$^{-1}$ and a maximum around 44 110 cm$^{-1}$, indicating that the 43 460-cm$^{-1}$ transition is polarized along the shorter molecular axis and the 44 110 cm$^{-1}$ along the longer one. The above observed results are compared with the calculated ones in Table I. The method of the calculation used here is already described elsewhere.[4,13-16] The long-axis-polarized 30 250- and 38 020-cm$^{-1}$ bands correspond to the calculated transitions, $S_1 \leftarrow S_0$ and $S_6 \leftarrow S_0$, respectively, and both bands are assigned to $^1B_{1u} \leftarrow {}^1A_g$. The 43 460- and 44 110-cm$^{-1}$ bands are assigned to $S_8 \leftarrow S_0$ ($^1B_{2u} \leftarrow {}^1A_g$) and $S_9 \leftarrow S_0$ ($^1B_{1u} \leftarrow {}^1A_g$) transitions, respectively.

The main contributor of the first excited state wave function, which corresponds to the observed 30 250-cm$^{-1}$ band, is $\chi_{8\text{-}9}(\pi)$, representing the one electron excitation configuration wave function from MO $\phi_8(\pi)$ to $\phi_9(\pi)$. The observed 38 020-cm$^{-1}$ band is regarded as a transition $\phi_{3'}(\pi') \leftarrow \phi_{2'}(\pi')$ and the 43 460-cm$^{-1}$ band as a superimposition of two transitions $\phi_9(\pi) \leftarrow \phi_6(\pi)$ and $\phi_{11}(\pi) \leftarrow \phi_8(\pi)$. The 44 110-cm$^{-1}$ band consists of $\phi_{12}(\pi) \leftarrow \phi_5(\pi)$ and $\phi_{11}(\pi) \leftarrow \phi_6(\pi)$. The MO's and the transition densities concerning the main contributors mentioned above are represented diagrammatically in Figure 3. The transition moment vectors on benzene and butadiyne fragments resulting from the respective transition densities are also shown by the transition density diagrams. It is seen from the MO diagram for the $S_1 \leftarrow S_0$ transition that the 30 250-cm$^{-1}$ band is regarded as a $\pi$-$\pi^*$ transition delocalized over the whole molecule. As explained in the Introduction, the transition densities give an aid to the classify the natures of electronic transitions after Platt's notation.[17] The transition density for the $S_1 \leftarrow S_0$ transition shows that the transition consists of a mixing of $^1L_a$ transitions of two benzenes and the transition of butadiyne, which gives a support for the prediction given in the introduction that the $S_1 \leftarrow S_0$ transition of diphenylbutadiyne is related to the $^1L_a$ band of phenylacetylene. The corresponding long axis polarized transition moment vectors on the terminal benzenes and butadiyne fragments are arranged colinearly with their directions being the same, and they interact in an attractive way. This is, as already discussed, the reason that the transition concerned is observed as the first band with lowest transition energy. In accordance with the above discussion, the position of this band for diphenylhexatriyne ($n = 3$) is largely red-shifted by 2850 cm$^{-1}$ compared with that for diphenylbutadiyne ($n = 2$).

Both MO diagram and transition density for $S_6 \leftarrow S_0$ transition show that the 38 020-cm$^{-1}$ band is assigned as a long-axis-polarized $\pi'$-$\pi'^*$ transition localized on the butadiyne moiety. The corre-

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**Table II.** Vibrational Analysis for the First $\pi$–$\pi^*$ Band System of Diphenylbutadiyne

| band (cm$^{-1}$) | diffrnce from the 0–0 band (cm$^{-1}$) | assignment | $\Delta\nu$ |
|---|---|---|---|
| 30 250[a] | | 0–0 | |
| 31 200 | 950 | 0–0 + 950[b] | |
| 31 810 | 1560 | 0–0 + 1560[b] | |
| 32 360 | 2110 | 0–0 + 2110[b] | |
| 33 310 | 3060 | 0–0 + 2110 + 950 | 0 |
| 33 930 | 3680 | 0–0 + 2110 + 1560 | −10 |
| 34 470 | 4220 | 0–0 + 2 × 2110 | 0 |
| 35 440 | 5190 | 0–0 + 2 × 2110 + 950 | −20 |
| 36 050 | 5800 | 0–0 + 2 × 2110 + 1560 | −20 |
| 36 580 | 6330 | 0–0 + 3 × 2110 | 0 |

[a] 0–0 transition; $^1B_{1u} \leftarrow {}^1A_g$. [b] $a_g$ modes.

sponding band for diphenylhexatriyne is also largely red-shifted by 3420 cm$^{-1}$ compared with that for diphenylbutadiyne.

The MO diagrams for $S_8 \leftarrow S_0$ transition elucidate that the 43 460-cm$^{-1}$ band has arisen from a mixing of the two types of intramolecular CT transitions (acetylene → terminal benzenes* and terminal benzenes → acetylene*), whose situation is, as described in the Introduction, just the same as that for the 279-nm $^1L_b$ band of phenylacetylene. The transition density for one type of CT transition is just the same as that for the other type of CT transition, each of which is localized on the terminal benzene fragments and, as also explained for phenylacetylene and diphenylhexatriyne, constitutes the short-axis-polarized $^1B_b$ terms with their moment vectors being the same in direction. The in-phase combination of the two kinds of CT transition moment vectors contributes to the intensity of the 43460-cm$^{-1}$ band. In contrast to the cases of the $S_1 \leftarrow S_0$ and $S_6 \leftarrow S_0$ transitions, the transition density and the transition moment vector for the $S_8 \leftarrow S_0$ transition have no contribution from the central butadiyne moiety, which predicts the transition energies for the above-mentioned CT bands of diphenylpolyyne ($C_6H_5$—$(C{\equiv}C)_n$—$C_6H_5$) to be rather insensitive to the variation of $n$. This prediction is proven from the fact that the band position of the CT band is 43 460 cm$^{-1}$ for diphenylbutadiyne and 44 000 cm$^{-1}$ for diphenylhexatriyne,[4] the difference being only 540 cm$^{-1}$. The 44 110-cm$^{-1}$ band is due to a localized electronic transition within the two phenyl rings which is polarized along the long axis.

**Vibrational Analysis of the First Electronic Band System.** In Table II the results of the vibrational analysis for the first electronic band system are shown. The 32 360-, 34 470-, and 36 580-cm$^{-1}$ bands are assigned as 0–0(30 250 cm$^{-1}$) + 2110, 0–0 + 2 × 2110, and 0–0 + 3 × 2110 cm$^{-1}$, respectively. The fundamental vibration of 2110 cm$^{-1}$ may be the totally symmetric ($a_g$) C≡C stretching mode.[18] Other than the 2110-cm$^{-1}$ mode, 950 and 1560 cm$^{-1}$ totally symmetric fundamentals are found. These fundamentals may correspond to the C═C stretching modes of monosubstituted benzenes.

**Solvent and Temperature Dependences of the Intensity of Each Band System.** As described above, the relative intensities of electronic bands of diphenylbutadiyne are not changed greatly by changes in the solvent polarities. At room temperature, if we change the media from ordinarily used liquid solvents such as ethanol to polymer matrices such as polyethylene, this tendency is also kept. But at a low temperature, the relative intensity of each electronic band is changed significantly (Figures 1 and 4); i.e., the intensities of the 30 250-, 43 460-, and 44 110-cm$^{-1}$ bands are heightened with a lowering of the temperature, but the intensity of the 38 020-cm$^{-1}$ band is lowered. As may be inferred from the temperature dependence of the Shpol'skii effect given in ref 8, these changes would be more effectively detected on further lowering of the temperature. This may suggest that the 38 020-cm$^{-1}$ band is due to a different kind of electronic transition from that of the other three bands. Especially, the intensity of the 30 250-cm$^{-1}$ band system is greatly heightened with a lowering of the temperature. The increase in intensity may be due to a weak Shpol'skii effect.[5,6] On the other hand, the 38020-cm$^{-1}$ band behaves in opposition to the Shpol'skii effect. The reason for these phenomena is not clear, but the following model might be considered for the interpretation. That is, the molecules adsorbed in the polyethylene matrix combine with the polymer through an interaction of the $\pi'$ orbital and hydrogen atoms of diphenylbutadiyne with the $\sigma$ framework of the polymer including the hydrogen atoms. Thus, the $\pi$ electronic system, which is perpendicular to the $\pi'$ and $\sigma$ electronic system, behaves as an isolated molecule and each $\pi$–$\pi^*$ band becomes sharper with lowering temperature. On the other hand, the intensity of the $\pi'$–$\pi'^*$ band is lowered with lowering temperature, since the $\pi'$ electronic system is used for the weak linkage with the polymer. In other words, each $\pi$–$\pi^*$ band may be considered as having mainly a nonphonon band character and the $\pi'$–$\pi'^*$ band as having mainly a phonon band character, since the effect of the guest–host coupling characteristic for the phonon band is only manifest in the latter band. On lowering the temperature, the weak bonding between $\pi'$ and the polymer may be strengthened to some degree due to thermodynamical stability of the geometrical arrangement of the interacting systems.

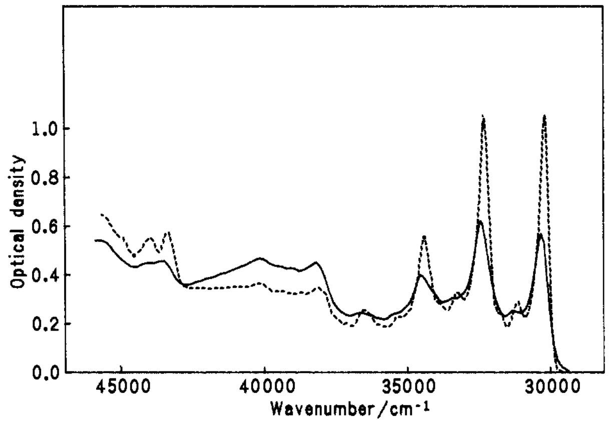
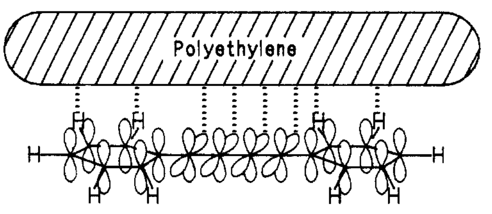


**Figure 4.** The absorption spectra of diphenylbutadiyne in an unstretched polyethylene matrix at room temperature (—) and at 97 K (---).



In order to get more detailed knowledge of the above consideration, we performed modified PPP calculations. In this MO calculation, the effect of the weak linkage between the guest and host molecules on the $\pi'$ electronic system is regarded as an inductive one, and the valence state ionization energy of the $2p_y$ atomic orbital is increased by 0.5–1.0 eV from the ordinarily used value. Here, we have assumed that the $\pi'$ orbital interacts with the hydrogen atom, which is charged $\delta+$, of the polymer. Thus, the effective nuclear charge of the carbon atom on $\pi'$ is increased by the electron-accepting nature of the hydrogen atom of the polymer molecule. If we adopt the concept of the variable electronegativity theory by Brown and Heffernan,[19] the ionization energy from the $2p_y$ orbital of the carbon atom on $\pi'$ may be increased as a result of a weak bonding between $\pi'$ and the polymer. The calculated results, thus obtained, explain the above-described guest–host intermolecular interaction model. That is, according to Table III, the intensity of the $S_6 \leftarrow S_0$ transition corresponding to the observed 38 020-cm$^{-1}$ band decreases with an increase in the value of Ip($2p_y$). By using the present guest–host intermolecular interaction model, we might explain the reason

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**Table III.** Changes in Calculated Transition Energies and Intensities of the First and Second Electronic Transitions for Variation of Ip(2py)

| | Ip($2p_y$) = 11.22 eV | | Ip($2p_y$) = 11.72 eV | | Ip($2p_y$) = 12.22 eV | |
|---|---|---|---|---|---|---|
| | $f$[a] | ($\Delta E$)[b] | $f$ | ($\Delta E$) | $f$ | ($\Delta E$) |
| $S_1 \leftarrow S_0$ | 1.332 | (27 720 cm$^{-1}$) | 1.346 | (27 760 cm$^{-1}$) | 1.368 | (27 720 cm$^{-1}$) |
| $S_6 \leftarrow S_0$ | 1.225 | (41 650 cm$^{-1}$) | 1.051 | (42 350 cm$^{-1}$) | 0.841 | (42 490 cm$^{-1}$) |

[a] Oscillator strength. [b] Transition energy.

**Table IV.** Comparison of the Calculated and Experimental Results for a Series of Diphenylpolyynes

| | first $\pi$-$\pi^*$ transition | | | | lowest $\pi'$-$\pi'^*$ transition | | | |
|---|---|---|---|---|---|---|---|---|
| | calcd | | obsd[d] | | calcd | | obsd[d] | |
| $n$[a] | $\Delta E$[b] (cm$^{-1}$) | $f$[c] | $\Delta E$ (cm$^{-1}$) | $\epsilon$[e] (10$^4$) | $\Delta E$ (cm$^{-1}$) | $f$ | $\Delta E$ (cm$^{-1}$) | $\epsilon$ (10$^4$) |
| 1 | 31 090 | 1.201 | 33 430 | 4.45 | 52 190 | 1.131 | | |
| 2 | 27 720 | 1.332 | 30 450 | 4.40 | 41 650 | 1.225 | 38 490 | 4.35 |
| 3 | 25 300 | 1.262 | 27 860 | 4.25 | 35 100 | 2.589 | 35 220 | 4.65 |
| 4 | 23 640 | 1.115 | 25 110 | 4.20 | 31 090 | 3.619 | 32 580 | 4.90 |
| 6 | 21 410 | 0.831 | 21 640 | 3.90 | 26 590 | 5.377 | 28 290 | 4.95 |
| 8 | 19 980 | 0.463 | 19 660 | 3.15 | 24 160 | 7.011 | 26 480 | 5.15 |

[a] Number of the triple bond. [b] Transition energy. [c] Oscillator strength. [d] Taken from ref 10. [e] Molar extinction coefficient determined at the 0–0 band.

for the so-called Shpol'skii effect. That is, if this is the case, in Shpol'skii media, the guest molecules interact with the host molecules through their $\sigma$ electron systems so that the $\pi$ electron systems of the guest molecules behave as those of isolated molecules.

The relative intensity of the $\pi'$-$\pi'^*$ band at 38 020 cm$^{-1}$ is lowered with lowering temperature, this being opposed to a so-called Shpol'skii effect. The reason of this phenomenon may be interpreted as follows. The unperturbed excited state total wave functions $\Psi_1$(unperturbed) and $\Psi_6$(unperturbed), corresponding respectively to the observed 30 250- and 38 020-cm$^{-1}$ bands, are

$$\Psi_1(\text{unperturbed}) = 0.162\chi_{7-10}(\pi) + 0.960\chi_{8-9}(\pi) + 0.197\chi_{2'-3'}(\pi') + \ldots$$

$$\Psi_6(\text{unperturbed}) = 0.283\chi_{4-9}(\pi) + 0.100\chi_{5-12}(\pi) + 0.171\chi_{7-10}(\pi) + 0.192\chi_{8-9}(\pi) + 0.283\chi_{8-13}(\pi) + 0.864\chi_{2'-3'}(\pi') + \ldots$$

and the perturbed ones, in which the effect of the weak linkage between the $\pi'$ electronic system and the polymer is taken into account as of inductive described above, are

$$\Psi_1(\text{perturbed}) = 0.163\chi_{7-10}(\pi) + 0.962\chi_{8-9}(\pi) + 0.183\chi_{2'-3'}(\pi') + \ldots$$

$$\Psi_6(\text{perturbed}) = 0.359\chi_{4-9}(\pi) + 0.179\chi_{5-12}(\pi) + 0.179\chi_{6-11}(\pi) + 0.228\chi_{7-10}(\pi) + 0.163\chi_{8-9}(\pi) + 0.359\chi_{8-13}(\pi) + 0.769\chi_{2'-3'}(\pi') + \ldots$$

Here, $\chi_{i-j}(\pi)$ (or $\chi_{i'-j'}(\pi')$) represents the configuration wave function of one-electron excitation from the occupied $\pi$ MO $\phi_i$ (or $\pi'$ MO $\phi_{i'}$) to the vacant $\pi$ MO $\phi_j$ (or $\pi'$ MO $\phi_{j'}$). As seen from the above total wave functions, $\Psi_1$(perturbed) is almost unchanged compared with $\Psi_1$(unperturbed). It is noted that the contributions of higher energy configurations increase on going from $\Psi_6$(unperturbed) to $\Psi_6$(perturbed). That is, the contributions of $\chi_{2'-3'}(\pi')$ and $\chi_{8-9}(\pi)$ to $\Psi_6$(perturbed) decrease in comparison with the case of the unperturbed one, while those of higher energy configurations increase. Since the transition moment vectors for $\chi_{2'-3'}(\pi')$ and higher energy configurations interact with each other with their moment vectors being opposite in direction and cancelled in parts, the above-mentioned increased contributions of higher energy configurations in $\Psi_6$(perturbed) caused perturbationally by lowering the temperature result in the increased degree of cancellation of the interacting transition moment vectors concerned, leading to the decrease in intensity of the $\Psi_6(\pi'$-$\pi'^*)$ band at 38 020 cm$^{-1}$.

Figure 5 shows the absorption spectra of diphenylbutadiyne in the stretched polyethylene film at room temperature and at 97 K. According to Figure 5a, the intensity of the 30 250-cm$^{-1}$ band is heightened with lowering temperature, while that of the 38 020-cm$^{-1}$ band is almost constant. In the case of Figure 5b, the increase in intensity of the 30 250-cm$^{-1}$ band is not so great compared with the case of Figure 5a, and the intensity of the 38 020-cm$^{-1}$ band is conversely lowered with decreasing temperature. From the above experimental results, we might say that, as in the case of the diphenylbutadiyne–polyethylene system showing a very weak Shpol'skii effect, the degree of the effect is strengthened by using oriented molecules in the stretched polymer film and a polarized light.

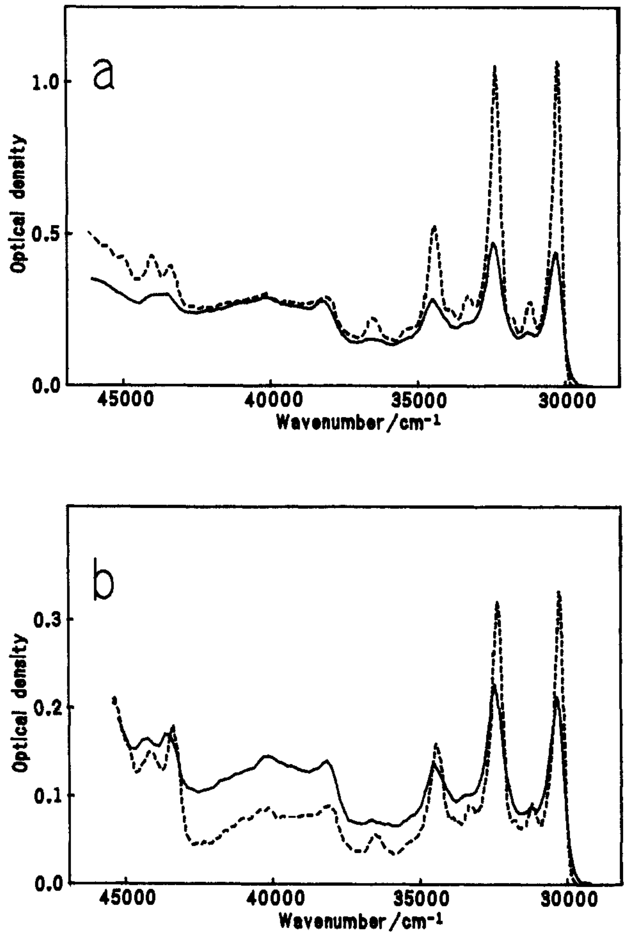

**Figure 5.** The absorption spectra of diphenylbutadiyne in the stretched polyethylene film at room temperature (—) and at 97 K (---). Parts a and b are measured with polarized light beams whose electric vectors are parallel to and perpendicular to the stretched direction of the film, respectively.

**$\pi$-$\pi^*$ and $\pi'$-$\pi'^*$ Transitions in Other Diphenylpolyynes.** As mentioned above, the second electronic band of diphenylbutadiyne is assigned to a $\pi'-\pi'^*$ transition. In order to ascertain existences of $\pi'-\pi'^*$ transitions in other diphenylpolyynes ($C_6H_5—(C\equiv C)_n—C_6H_5$, $n = 1 \sim 8$), modified PPP calculations are performed, and the results are shown in Table IV together with the experimental ones.[10] The calculated first and second transition energies decrease with increasing $n$. The intensity of the first transition decreases slightly with increasing $n$, while that of the second one increases remarkably.[4] These calculated results accord perfectly with the experimental ones obtained by Armitage et al.[10] The first electronic band of each compound is due to a $\pi-\pi^*$ transition and the second one to a $\pi'-\pi'^*$ transition.

## IV. Conclusion

Diphenylpolyynes have two kinds of $\pi$ electronic systems, $\pi$ and $\pi'$, which are mutually perpendicular. Therefore, the polyynes may show $\pi'-\pi'^*$ bands other than ordinarily observed $\pi-\pi^*$ bands. The 38 020-cm$^{-1}$ band of diphenylbutadiyne has been assigned to a $\pi'-\pi'^*$ transition from its location, intensity, polarization, and temperature dependence of the band intensity. The 38 020-cm$^{-1}$ band behaves in opposition to the Shpol'skii effect; i.e., the intensity of the band decreases with decreasing temperature, while that of the 30 250-cm$^{-1}$ band, which is assigned to the first $\pi-\pi^*$ transition, increases. We may explain the above experimental facts by considering a weak interaction between the $\pi'$ (and $\sigma$) electronic system of diphenylbutadiyne and the $\sigma$ electronic system of the polymer molecule. That is, in this system the guest molecule combines with the host one in such a manner that the $\pi$ electronic system cannot interact with the $\sigma$ framework of the host molecule. As a result, the $\pi$ electronic system of the guest molecule behaves as that of an isolated gas molecule. This might be an explanation for the reason of the Shpol'skii effect. In order to ensure the above explanation for the Shpol'skii effect, it is necessary to accumulate experimental data about compounds having two kinds of $\pi$ electronic systems, $\pi$ and $\pi'$. Furthermore, in the present MO calculations, the interaction between $\pi'$ and $\sigma$ electronic systems in diphenylbutadiyne was neglected, but it might be necessary to take account of the effect of it in the MO calculations.

**Registry No.** Diphenylbutadiyne, 886-66-8.

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# Gas-Phase Reactivity of the HCO Radical with Unsaturated Hydrocarbons: An Experimental and Theoretical Study

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**Abstract:** The kinetics and mechanism of the reactions of HCO radicals with a series of unsaturated hydrocarbons were studied experimentally by the flash photolysis-laser resonance absorption technique and theoretically, in the particular case of ethylene, by ab initio SCF MO calculations with double $\zeta$ basis sets. Experiments were carried out in the temperature range 350–510 K by photolyzing acetaldehyde for the generation of HCO. The Arrhenius expressions obtained are the following, in cm$^3$·molecule$^{-1}$·s$^{-1}$ units: ethylene, $(1.5 \pm 0.6) \times 10^{-13}\exp[-(2750 \pm 75\ K/T)]$; propene, $(1.7 \pm 0.9) \times 10^{-13}\exp[-(2700 \pm 100\ K/T)]$; isobutene, $(5.45 \pm 2.9) \times 10^{-13}$, $\exp[-(3125 \pm 130\ K/T)]$; 1-butene, $(3.8 \pm 2.7) \times 10^{-13}\exp[-(3000 \pm 180\ K/T)]$; 2-butene, $(3.3 \pm 2.8) \times 10^{-13}\exp[-(3000 \pm 220\ K/T)]$; and 1,3-butadiene, $(5.8 \pm 1.3) \times 10^{-13}\exp[-(2050 \pm 50\ K/T)]$. The uncertainties quoted are equal to $2\sigma$. The reactivity of the HCO radical with respect to that of unsaturated hydrocarbons is compared to that of other radicals. The end-product analysis in the photolysis of the acetaldehyde–olefin (or butadiene) system has shown that the reaction essentially proceeds via an addition mechanism, rather than a hydrogen atom transfer from HCO to the double bond, which is also energetically favorable. This is the first characterized reaction of HCO which does not involve such a hydrogen transfer from the radical. These results are supported by quantum mechanical calculations of the potential energy surfaces involved in the two possible reaction channels. These calculations show in particular that the energy barrier is much higher for the hydrogen atom transfer channel than for the addition process. In addition, calculated activation energies and preexponential factors are in good agreement with experimental results.

The formyl radical is an important intermediate in the chemistry and photochemistry of aldehydes in the gas phase and in oxidizing systems involving hydrocarbons. However, little is known to date concerning its reactivity. The main reaction of HCO in the oxidation of hydrocarbons, either in combustion or in atmospheric processes, is the fast reaction with molecular oxygen yielding CO and the $HO_2$ radical. The rate constant for this reaction, along with that for the similar reaction of HCO with NO, has been measured by several authors.[1]

$$HCO + O_2 \rightarrow CO + HO_2 \qquad \Delta H = -32\ \text{kcal·mol}^{-1} \quad (1)$$

$$HCO + NO \rightarrow CO + HNO \qquad \Delta H = -33\ \text{kcal·mol}^{-1} \quad (2)$$

$$k_1 = 5.5 \times 10^{-12},$$

$$k_2 = 1.2 \times 10^{-11}\ \text{cm}^3\text{·molecule}^{-1}\text{·s}^{-1}\ \text{at 298 K}$$

In the absence of oxygen (in the photochemistry of aldehydes for example) HCO reacts essentially with itself or with other radicals (H, $CH_3$, ...).

$$HCO + HCO \rightarrow CO + HCHO \qquad \Delta H = -70\ \text{kcal·mol}^{-1} \quad (3)$$

$$HCO + H \rightarrow CO + H_2 \qquad \Delta H = -87\ \text{kcal·mol}^{-1} \quad (4)$$

$$HCO + CH_3 \rightarrow CO + CH_4 \qquad \Delta H = -87\ \text{kcal·mol}^{-1} \quad (5)$$

All these reactions are fast: $k = 3\text{–}11 \times 10^{-11}$ cm$^3$·molecule$^{-1}$·s$^{-1}$ at room temperature.

Hydrogen abstraction by the HCO radical from molecules is highly unlikely because of the relatively weak C–H bond formed in formaldehyde: D(H–CHO) = 87 kcal·mol$^{-1}$. Most hydrogen

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(1) Temps, F.; Wagner, H. Gg. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 410. Langford, A. O; Moore, C. B. *J. Chem. Phys.* **1984**, *80*, 4211 and references therein.