Dimer Formation of 9-Cyanoanthracene in a Nonpolar Medium at Low Temperatures

Toshihiko Hoshi,* Jun Okubo,† Fumitoshi Imaizumi, Isao Ono,
Michio Kobayashi,†† and Hiroyasu Inoue†††
Department of Chemistry, College of Science and Engineering,
Aoyama Gakuin University, Setagaya-ku, Tokyo 157
† Department of Natural Science for General Education, Faculty of Engineering,
Tokyo Denki University, Inzai-machi, Inba-gun, Chiba 270-13
††Department of Chemistry, Nagaoka University of Technology, Nagaoka 940-21
†††Department of Applied Chemistry, Faculty of Technology, Kanagawa University,
Kanagawa-ku, Yokohama 221
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The polarized electronic absorption spectrum of 9-cyanoanthracene has been measured in a stretched poly(vinyl alcohol) (PVA) film at 101 K, and the polarizations of the electronic transitions determined. It was found that the longer-molecular-axis polarized bands are at 364.4, 262.1, and 229 nm, and that the shorter-molecular-axis polarized ones are at 411.2 and 223 nm. The absorption spectra of 9-cyanoanthracene were measured in MP (a 1:1 mixed solvent of methylcyclohexane and isopentane) at room and lower temperatures. It was found that additional bands appear at the lower energy sides of the corresponding monomer bands at lower temperatures. These spectral changes may be interpreted as being due to dimer formation. The dimer may be stabilized mainly through dipole–dipole interactions between the two cyano groups taking on a C_{2h} symmetry. The 412.5, 363.5 and 281.5 nm bands of the dimer are assigned to the calculated $S_1 \leftarrow S_0$ ($B_u \leftarrow A_g$), $S_4 \leftarrow S_0$ ($A_u \leftarrow A_g$) and $S_8 \leftarrow S_0$ ($A_u \leftarrow A_g$) transitions, respectively; these transitions correspond to the $S_1 \leftarrow S_0$ ($A_1 \leftarrow A_1$), $S_2 \leftarrow S_0$ ($B_2 \leftarrow A_1$) and $S_3 \leftarrow S_0$ ($B_2 \leftarrow A_1$) transitions of the monomer.

It is well known that anthracene and its derivatives form two types of dimers caused by weak intermolecular interactions at low temperatures; one is called a sandwich dimer, and the other a stable dimer.[1-4] The sandwich-type dimer is obtained by a photochemical cleavage of the so-called photodimer in rigid glass at 77 K. The stable-type dimer is obtained when anthracene or its derivatives is dissolved in a nonpolar solvent and then slowly cooled.

Chandross and Ferguson reported that, in the case of 9-cyanoanthracene, even prolonged irradiation of its photodimer produced no sufficient concentration of the sandwich dimer to show a detectable absorption spectrum.[3] That is, the sandwich pair, which is produced by a photocleavage of the photodimer, easily returns to the original photodimer. Recently, Sixl et al. clarified the mechanism of the photochemical and thermal reaction processes concerning interconversion between the photo- and sandwich-dimers of 9-cyanoanthracene from measurements of the ESR and time-resolved absorption spectra.[5] According to them, for instance, the activation energy for the dissociation of the photodimer into the monomer pair can be estimated to be 1.67 eV. It is known that the photodimer of 9-cyanoanthracene is formed via its excimer state, as are those of other anthracene derivatives.[3] Based on the pressure dependence of excimer emissions from 9-cyanoanthracene crystals, Brillante et al. have reported that a head-to-head type excimer is formed at pressure lower than 8 kbar, and that a head-to-tail type at greater than 8 kbar.[6] However, only the head-to-tail type excimer can change into the photodimer. As described above, although detailed investigations concerning the formation of the photodimer, sandwich dimers, and excimers have been carried out for 9-cyanoanthracene, few descriptions have appeared for stable dimers.

In the present investigation, the electronic absorption spectra of 9-cyanoanthracene were measured in a polyethylene (abbreviated to PE) film, and in a 1:1 mixed solvent of methylcyclohexane and isopentane (MP) at various temperatures. From these spectral data together with MO calculations, we now discuss the mechanism of weak intermolecular interactions concerned with the dimer formation of 9-cyanoanthracene. Furthermore, the polarized absorption spectrum of the compound was measured in a stretched polymer film in order to determine the nature of the electronic transitions, which may provide helpful information to clarify the electronic nature of the dimer.

Experimental

Materials. Commercially available 9-cyanoanthracene (Aldrich Chemical Co.) was recrystallized three times from ethanol. Cyclohexane (Wako Pure Chemical Industries, Ltd.) was distilled after removal of benzene through a silica-gel column. Methylcyclohexane (Dojin Chemical Co., Sp. Grade) and isopentane (Wako) were distilled after reflux with sodium metal. PE films (Okura Kogyo Co.) were soaked in cyclohexane for one or two day(s) in order to remove any impurities.

Measurements. The absorption spectra in solutions and polymer films were recorded on a Shimadzu UV 360 type spectrophotometer equipped with an N_2-chryostat. The polarized absorption spectra were measured with the aid of a stretched-polymer-film technique.[7,8]

MO Calculation

MO calculations were performed using a modified PPP method, which can be applied to three-dimensionally extended π electronic systems, such as in the cases of the sandwich dimers treated here.[9-13] The valence-state ionization energies (I_p(r)) and electron affinities (E_a(r)) for the carbon and nitrogen atoms used are: I_p(C)=11.22 eV, I_p(N)=14.16 eV, E_a(C)=0.62 eV, and E_a(N)=1.67 eV. The resonance integrals between adjacent atoms in the same molecular plane are calculated by means of a variable β approximation, after Nishimoto and Forster;[14] the integrals β_{rs} between the atoms belonging to different molecules from each other are estimated from the relation $\beta_{rs}=0.3541 S_{rs}(I_p(r)+I_p(s))$.[11] Here, S_{rs} is an overlap integral between adjacent atoms, r and s. In CI calculations, 64 singly electronic excited configurations were taken into account for 9-cyanoanthracene and its dimer.

Results and Discussion

It has been found that the irradiation of a saturated acetonitrile solution of 9-cyanoanthracene gives rise to dimerization, producing a so-called photodimer.[5] As described in the introductory section, illumination of the above-mentioned photodimer in a low-temperature matrix does not give any dimers formed through weak intermolecular forces, this being in contrast with cases of the other anthracene derivatives.[3] However, the present experiment, as described later, shows that a new band appears at the longer wavelength side of the first absorption band of the monomer in a low-temperature MP solution. The appearance of the new band may be due to weak intermolecular interactions.

Electronic Transitions of the Monomer. Figure 1 shows the polarized absorption spectrum of 9-cyanoanthracene measured in a stretched PVA films at 101 K. In this figure, $D_{\parallel}$ and $D_{\perp}$ are the absorbances measured with light beams polarized along parallel and perpendicular to the stretched direction of the PVA film, respectively. Rd is the ratio of $D_{\parallel}$ and $D_{\perp}$ (Rd=$D_{\parallel}/D_{\perp}$). Rs is the ratio of stretching.[7,8] In the wavelength region 320—430 nm, two kinds of band systems are found, i.e., those consisting of three apparent broad peaks at 411.2, 390.5, and 370.5 nm, and relatively sharp peaks at 364.4 and 346.8 nm. The broad band system originated at 411.2 nm and the sharp one at 364.4 nm are polarized along the shorter- and longer-molecular axes, respectively; this is because the broad 411.2 nm band system has relatively low Rd values, whereas the Rd curve shows maxima at the sharp 364.4 and 346.8 nm band positions. This indicates that the above-mentioned two-band systems are due to different electronic transitions. The most intense 262.1 nm band with the highest Rd values and relatively weak 223 nm one with the lowest Rd values are polarized along the longer- and shorter-molecular axes, respectively. Furthermore, one can find very weak shorter- and longer-axes polarized bands at 236 and 229 nm, respectively, the polarizations being determined from the behaviors of the Rd, $D_{\parallel}$, and $D_{\perp}$ curves. These observed results are compared with MO calculated ones in Table 1. The longer-axis-polarized bands at 364.4, 262.1, and 229 nm are assigned to the transitions from S_0 to S_2, S_6, and S_9, respectively, and the shorter-axis polarized ones at 411.2, 236, and 223 nm to S_1, S_8, and S_{11}. Other than the above-mentioned observed bands, a

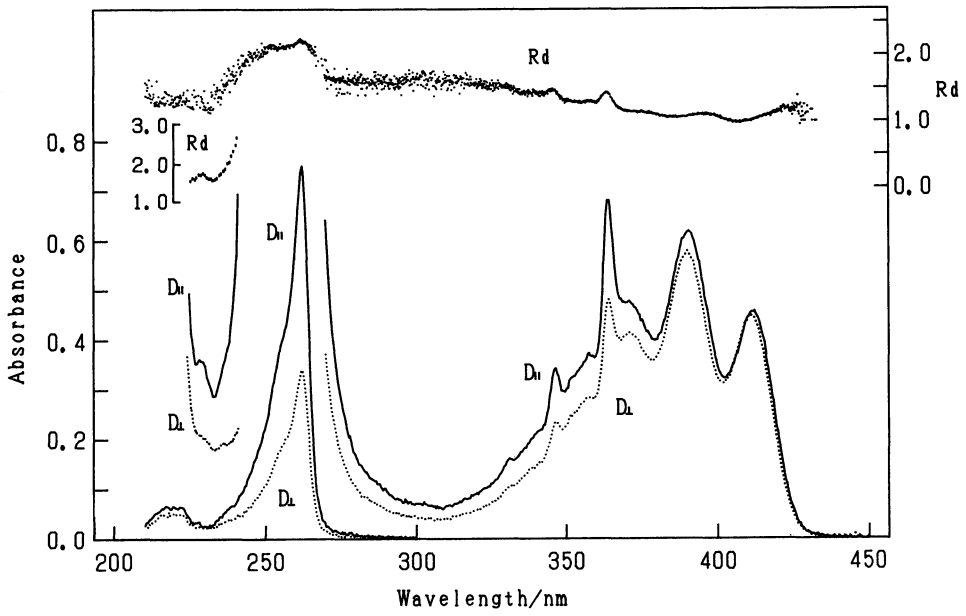

Fig. 1. The polarized absorption spectrum of 9-cyanoanthracene in the stretched PVA film at 101 K. Rs=5.2

Table 1. Comparison of the Calculated and Observed Results for the $S_n \leftarrow S_0$ Transitions of 9-Cyanoanthracene

	Transition energy (nm)		Intensity		Polarization direction	
	Calcd	Obsd[a]	Calcd[b]	Obsd[c]	Calcd	Obsd[a]
S_1 ($^1A_1$)	400.0	411.2	0.4036	0.028	Z	Z
S_2 ($^1B_2$)	373.4	364.4	0.0045	(ca. 0.01[d])	Y	Y
S_3 ($^1B_2$)	293.7	285	0.0140	0.004	Y	—
S_4 ($^1A_1$)	277.4		0.0009		Z	
S_5 ($^1B_2$)	277.0		0.0174		Y	
S_6 ($^1B_2$)	269.1	262.1	2.3094	1.000	Y	Y
S_7 ($^1A_1$)	259.6	236	0.0317	0.071	Z	Z
S_8 ($^1A_1$)	252.8		0.0520		Z	
S_9 ($^1B_2$)	225.5	229	0.0359	0.075	Y	Y
S_{10}($^1A_1$)	220.2		0.0315		Z	
S_{11}($^1A_1$)	219.3	223	0.2001	0.110	Z	Z
S_{12}($^1A_1$)	214.5		0.0585		Z	
S_{13}($^1A_1$)	204.0		0.0000		Z	

a) Observed in the PVA matrix at 101 K. b) Oscillator strength. c) Relative intensities with respect to the 262.1 nm band. d) Estimated from the reduced polarization spectrum. Y: Perpendicular to the C_2 axis in the molecular plane. Z: The C_2 axis.

band corresponding to the calculated $S_3 \leftarrow S_0$ transition might be found at the lower energy side of the strong 262.1 nm band. Although the presence of this band is not clear in the polarized absorption spectrum shown in Fig. 1, a comparison of the spectra of the monomer and the dimer (shown in the next section) may indicate the existence of a weak band around 285 nm. In fact, by carefully inspecting the spectrum shown in Fig. 1, one might find a very weak shoulder at around 285 nm.

Temperature Dependence of Absorption Spectrum: Dimer Formation. The absorption spectra of 9-cyanoanthracene were measured in MP at various temperatures for the lower energy electronic bands, and are shown in Fig. 2. Each band is intensified and sharpened with a lowering of the temperature from room temperature to 124 K with isosbestic points (Fig. 2a). Although the first two peaks are red-shifted by ca. 3 nm at a lower temperature, the others are not shifted (Fig. 2a). This indicates that both the former peaks (401.8 and 380.7 nm at 124 K) and the latter ones (362.8, 345.2, and 329.5 nm) belong to different electronic band systems, supporting the above assignment described in Table 1. A decrease in temperature from 124 to 101 K results in further changes in the spectra with different isosbestic points from the above ones, and the emergence of additional new bands (412.5, 407.3, 390.0, 371.7, and 352 nm) at the lower energy side of the corresponding bands at 124 K (Fig. 2b). Furthermore, a shoulder and a considerable intense peak were found at 270 and 281.5 nm (Fig. 2b). These spectral changes may be due to the formation of a dimer caused by weak intermolecular interactions. If the above argument is the case, any additional bands ascribed to dimer formation would not be expected to appear, even at low temperature in rigid matrices, such as a PE film, in which the adsorbed molecules disperse monomolecularly.

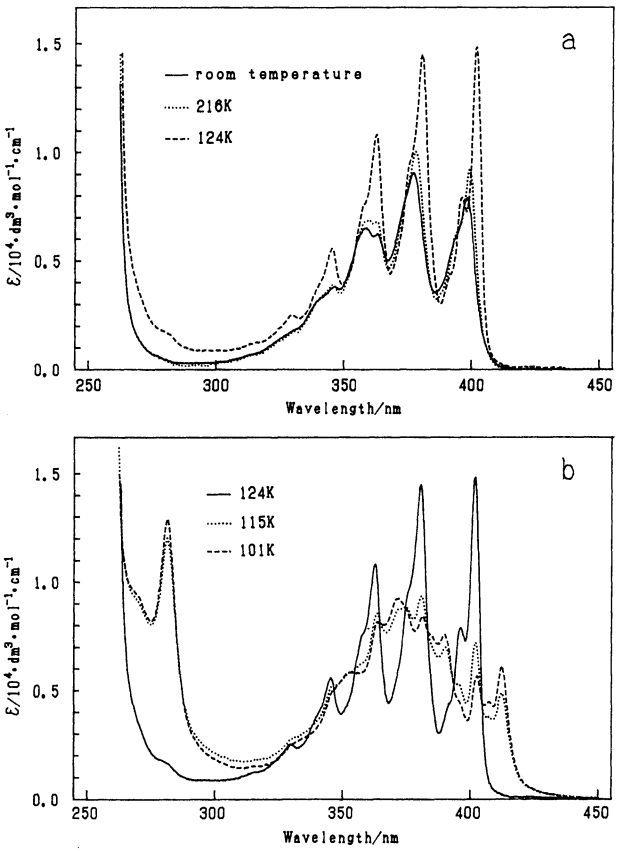

Fig. 2. The absorption spectra of 9-cyanoanthracene in MP at various temperatures.

Figure 3 shows the absorption spectra of 9-cyanoanthracene in a PE film at room temperature and 101 K. As can be seen from this figure, although each band is intensified with a decrease in temperature, no

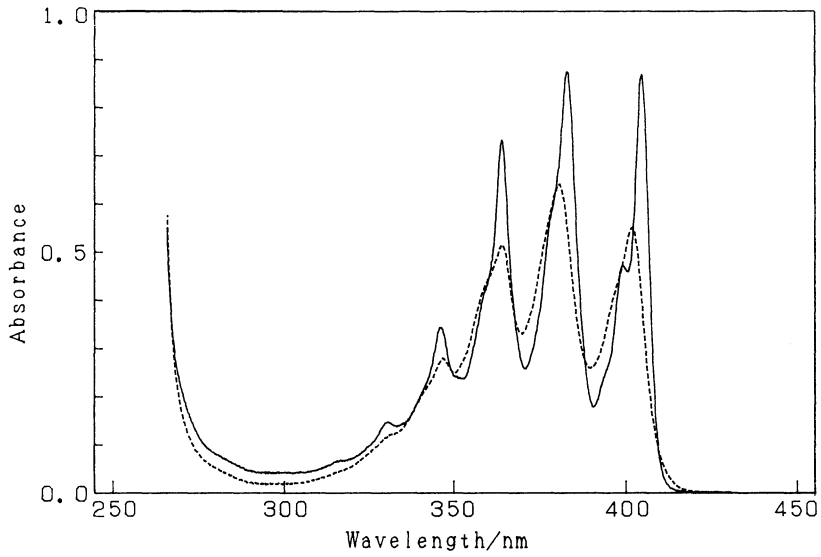

Fig. 3. The absorption spectra of 9-cyanoanthracene in the isotropic PE film at room temperature (----) and 101 K (——).

additional bands ascribable to the dimer emerge. This may be additional evidence that the bands at 412.5, 390.0, 371.7, 352, and 281.5 nm appearing in the low-temperature MP can be attributed to the dimer.

MO Calculation for the Dimer. In order to clarify the electronic structure and geomeotry of the dimer of 9-cyanoanthracene, MO calculations were performed. In these calculations, three structures (A, B, and C) were assumed (Fig. 4). Structure A is a sandwich type, and is considered to be stabilized through σ-bonding-type overlaps of the π-orbitals and weak dipole–dipole interactions. Structure B is of the C_{2v} sandwich type, whose stabilization energies depend only on the overlaping of the π-orbitals, while the dipole–dipole interactions rather act as repulsive forces. Structure C is of C_{2h} and the dimer is stabilized through a relatively strong dipole–dipole interaction, the dipole moment being mainly localized on the C≡N group. In the calculations, the distances between the two monomer-molecular planes were assumed to be 3.5 Å for structures A and C.[3] The corresponding distance for structure B

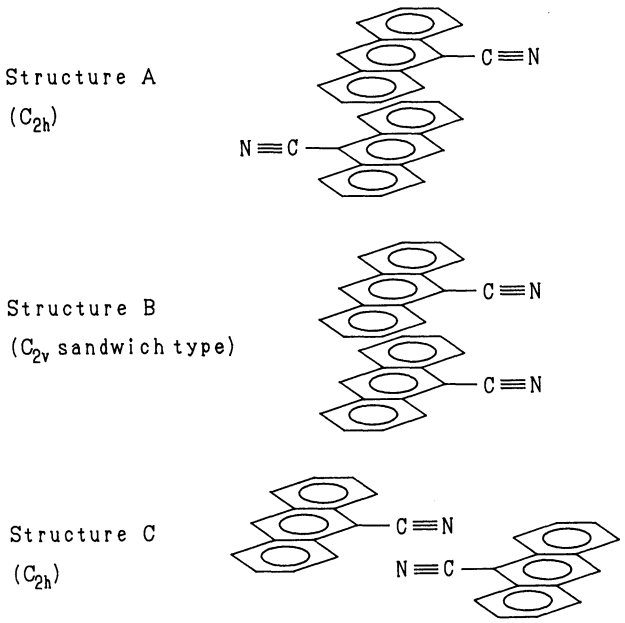

Fig. 4. Three assumed structures of 9-cyanoanthracene dimer.

Table 2. The First Three Calculated Transition Energies and Intensities of the Monomer and Dimer of 9-Cyanoanthracene

	Dimer										Monomer		
	Obsd		Calcd[f]								Calcd[g]		
			Structure A[e]			Structure B[e]			Structure C[e]				
	ΔE[a]	ε[b]	ΔE	I[c]		ΔE	I		ΔE	I		ΔE	I	
S_1	412.5	>6190[h]	446.7	Forb.[d]	A_g	417.0	0.000	B_2	397.4	0.954	B_u	392.5	0.468	A_1
S_2			390.8	0.012	B_u	381.0	0.850	A_1	387.8	Forb.	A_g	355.5	0.007	B_2
S_3			377.4	0.837	B_u	378.0	0.002	A_1	355.5	Forb.	B_g	289.2	0.026	B_2

a) Transition energy (nm) measured in MP at 101 K. b) Molar absorptivity ($dm^3\ mol^{-1}\ cm^{-1}$) measured in MP at 101 K. c) Oscillator strength. d) Forbidden. e) See text. f) 8×8 configurations are taken into account in CI calculation. g) 4×4 configurations are taken into account in CI calculation. h) The true ε-value is considered to be greater than this value.

was 4.0 Å, since, in this case, if we use a value of 3.5 Å, the interactions among the excited configurations are so strong that the S_1 state is computed below S_0. The calculated results for the three assumed structures are summarized in Table 2. If structure A is the case, the 412.5 nm dimer band can be assigned to the calculated $S_3 \leftarrow S_0$ transition, since the $S_1 \leftarrow S_0$ (446.7 nm, $A_g \leftarrow A_g$) transition is forbidden, and $S_2 \leftarrow S_0$ (390.8 nm, $B_u \leftarrow A_g$) only weakly allowed. However, the above-calculated results do not reproduce the observed ones, i.e., the first electronic band of the 9-cyanoanthracene monomer is red-shifted by dimer formation, but the corresponding calculated transition of the monomer is contrarily blue-shifted. The calculated results for structure B lead to an assignment in which the first electronic band (412.5 nm) of the dimer is ascribed to the calculated $S_2 \leftarrow S_0$ transition (381.0 nm, $A_1 \leftarrow A_1$). These calculated results do not also satisfy the observation, because in this model calculation the first electronic transition of the monomer is blue-shifted by dimer formation. On the other hand, in the case of structure C the calculated results explain the observation in a better way: the observed 412.5 nm dimer band is ascribed to the calculated $S_1 \leftarrow S_0$ transition (397.4 nm, $B_u \leftarrow A_g$), this transition being computed at the lower energy side of the $S_1 \leftarrow S_0$ one of the monomer.

According to Kobayashi, Kajimoto, Honma, and Tsuchiya, benzonitrile forms a dimer in a free jet.[15] The structure of the dimer is reported to be a planar form with two cyano groups facing each other in an antiparallel geometry. They have thought that a dipole–dipole interaction between the two cyano groups contributes, as a major force, to the stabilization energies of the dimer, to

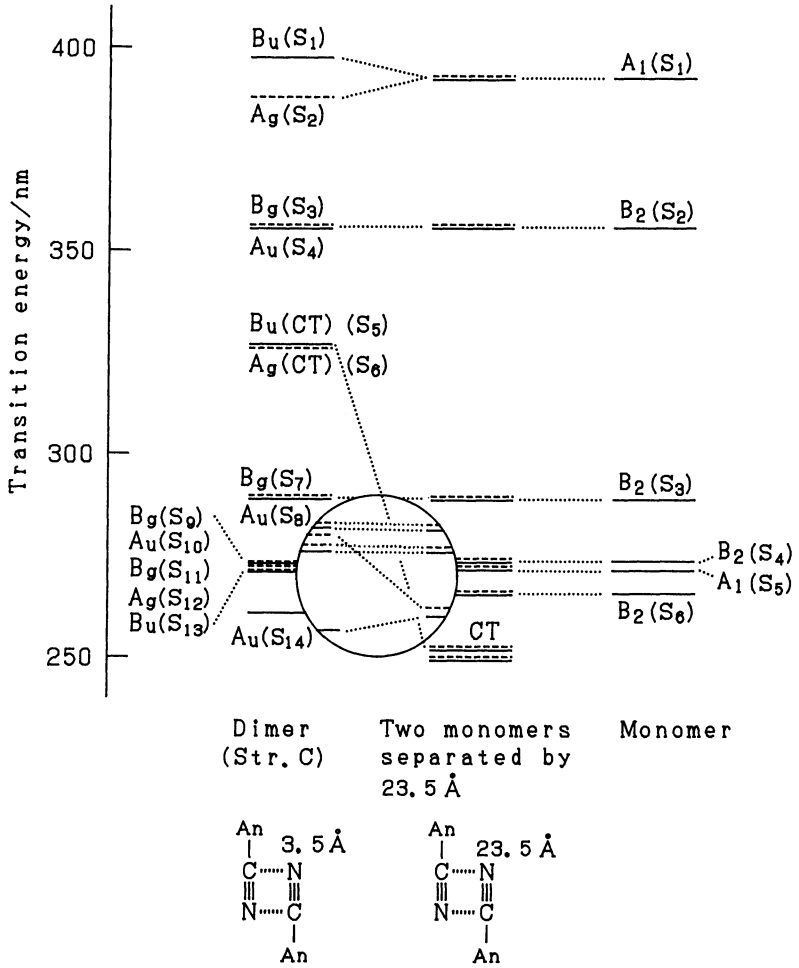

Fig. 5. The results of configuration analysis for 9-cyanoanthracene dimer. An: Anthryl (9-) group. Solid (—) and broken (----) lines represent allowed and forbidden transitions, respectively. The energy levels corresponding to the ith excited state wavefunction (ψ_i) are connected with those to the mainly contributed wavefunctions (ψ_g^0) of reference molecule (two monomers separated by 23.5 Å) by dotted lines (·····). All the main contributors contribute more than 99 per cent, except for the cases of S_9 ($\psi_9 = \psi_7^0$ (88.5%) + ψ_{11}^0 (11.5%)) and S_{11} ($\psi_{11} = \psi_7^0$ (88.5%) + ψ_{11}^0 (11.5%)).

which a weak hydrogen bonding interaction acts as a minor one. This hydrogen bonding, however, plays an important role in maintaining the planarity of the benzonitrile dimer. In the case of the 9-cyanoanthracene dimer, however, it is considered that the formation of hydrogen bonding may be impossible, because 9-cyanoanthracene has no hydrogen atom corresponding to the *o*-hydrogen atom of benzonitrile. 9-Cyanoanthracene can not, therefore, form a planar-type dimer

Nature of the Electronic Transitions of the Dimer. To determine the origin of the electronic transition of the dimer, we carried out a configuration analysis (CA);[16] the results are given in Fig. 5. In the CA calculation, two non-interacting monomers are used as a reference molecule, in which two monomers are placed in a C_{2h} symmetry, like structure C, and are separated by 23.5 Å in the intermolecular plane distances. For CI calculations of the dimer and the reference molecule, 64 excited configuration wavefunctions were taken into account. In a CI calculation for the monomer, 16 excited configuration wavefunctions were used, which correspond to the 64 ones of the dimer or the reference molecule. The short-axis-polarized $S_1 \leftarrow S_0$ transition (392.5 nm) of the monomer is split into allowed ($S_1 \leftarrow S_0$) and forbidden ($S_2 \leftarrow S_0$) transitions by dimer formation, the allowed one appearing at the lower energy side (397.4 nm) of the forbidden one (387.8 nm). The $S_6 \leftarrow S_0$ ($B_2 \leftarrow A_1$) monomer transition, corresponding to the observed longer-axis-polarized 261.9 nm band, is split into two dimer transition, $S_{11} \leftarrow S_0$ ($B_g \leftarrow A_g$, 272.4 nm) and $S_{14} \leftarrow S_0$ ($A_u \leftarrow A_g$, 261.1 nm) by the dimer formation. In this case, the allowed $A_u \leftarrow A_g$ transition is computed to be at the higher energy side of the forbidden one ($B_g \leftarrow A_g$). The second monomer electronic band at 362.8 nm in MP at 101 K (364.4 nm in the PVA film) is scarcely shifted, and appears at 363.5 nm due to dimer formation. According to the CA calculation shown in Fig. 5, the calculated $S_2 \leftarrow S_0$ monomer transition corresponding to the 362.8 nm monomer band is not shifted due to dimer formation, indicating that the observed 363.5 nm band can be assigned to the origin of the second electronic band system of the dimer. In the spectrum of the dimer there is a relatively strong band at 281.5 nm (Fig. 2b), which is assigned to the calculated $S_8 \leftarrow S_0$ ($A_u \leftarrow A_g$) dimer transition corresponding to the $S_3 \leftarrow S_0$ ($B_2 \leftarrow A_1$) transition of the monomer. Although the $S_3 \leftarrow S_0$ transition of the monomer is very weakly allowed, this transition is significantly intensified by dimer formation. Although the calculated $S_5 \leftarrow S_0$ ($B_u \leftarrow A_g$) and $S_6 \leftarrow S_0$ ($A_g \leftarrow A_g$) dimer transitions are both intermolecular charge transfer transitions between the two monomer molecules, the corresponding bands are not observed. The transition might be buried under the relatively strong first and second allowed electronic bands.

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