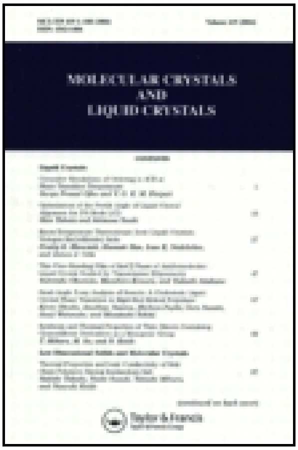

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Charge Transfer Transitions from Cyclohexadienyl-Type Radicals to Host Molecules in Anthracene Single Crystals

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Charge Transfer Transitions from Cyclohexadienyl-Type Radicals to Host Molecules in Anthracene Single Crystals

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The optical absorption spectra of 1-, 2- and 9-dibenzo-cyclohexadienyl radical in anthracene crystals have been obtained and analyzed. It is shown that the absorption lines consist of vibrational progression and charge-transfer lines for 2- and 9-DBCR. Each line belonging to the former has the same polarization as the most intense 0–0 vibrational line and the latter show polarization character depending on the direction of charge transfer and the transition energy was found to have a coulombic dependence on the distance of charge transfer. It is pointed out that only charge transfer lines were observed for 1-DBCR. The splitting of lines were observed and ascribed either to the resonance transfer interaction between two neighboring molecules situated at an equal distance from the radical or to the site symmetry. It is suggested that the intensity of the charge-transfer lines are borrowed from the intra-radical transition. The result that the charge transfer lines are more intense than the intra-radical lines for 1-DBCR was discussed.

I INTRODUCTION

Much attention has been paid on the electronic properties and energy transport in aromatic hydrocarbon single crystals.[1,2] For clarifying the electronic properties of such molecular crystals, the spectroscopic studies of impurity doped crystals have been found to play an important role. The optical transitions, which have been studied extensively concerning impurities in these crystals, however, have been mostly restricted to the intra-molecular transitions in the impurities or the host transitions perturbed by the impurities.[3] Little information has been obtained on the guest-host intermolecular transitions in these crystals. The excited states of such intermolecular transitions may be extended to the host molecules and may exhibit characters influenced by the host continuum states.

Recently the present authors have observed guest-host intermolecular transitions from the hydronaphthyl radicals to host molecules in naphthalene single crystals.[4] The radical, which is produced in naphthalene crystals by ionizing radiation, is a cyclohexadienyl-type radical and involves hydrogen atom attached to a naphthalene molecule. Two hydrogen atoms combined to a carbon atom through hyperconjugation form a pseudo-π orbital and the addition of such an orbital to a naphthalene molecule produces a new level in the forbidden gap in naphthalene crystal. Since this level is half-filled, both electron and hole transfers from the radical to host molecules may be expected. The optical absorption associated with the radical has been found to have a series of sharp lines with polarization different from the most intense 0–0 vibrational line, in addition to the vibrational progression which has the same polarization as the 0–0 vibrational line. Each line has been assigned to a charge transfer transition from the radical to one of the molecules around the radical by considering that the polarization of the absorption line agree with the direction of the charge transfer and the charge transfer to nearer molecules shows smaller transition energies. Such an assignment results in a relation between the transition energy E and the distance r between the radical and the molecule to which the charge transfer takes place:

$$E = E_{\infty} - \frac{e^2}{\varepsilon r}, \tag{1}$$

where ε is the dielectric constant and E_{∞} is a constant.

The qualitative features of the charge transfer transition have been explained as follows.[4] The energy of the charge transfer transitions is smaller than the energy of the charge transfer to the infinitely separated molecule by the coulombic attraction between the charged radical and the transfered carrier. According to the molecular orbital calculation,[5] the half-filled level of the radical is situated near the middle of the forbidden gap, as schematically shown in Figure 1, and therefore strong configuration mixing between the charge transfer of a positive hole (a) and an electron (b) may arise. This configuration mixing may explain the experimental observation that the phonon coupling of the charge transfer transition is much smaller than normally expected for a charge transfer transition.[6] The intensity of the charge transfer transition may be borrowed from the intra-radical transition. Salient features of such charge transfer transitions are that the wave function of the charge-transfer excited state is much localized in a specific molecule rather than extending to several molecules. It has been shown that the splitting of some charge transfer transitions and the delocalization of some

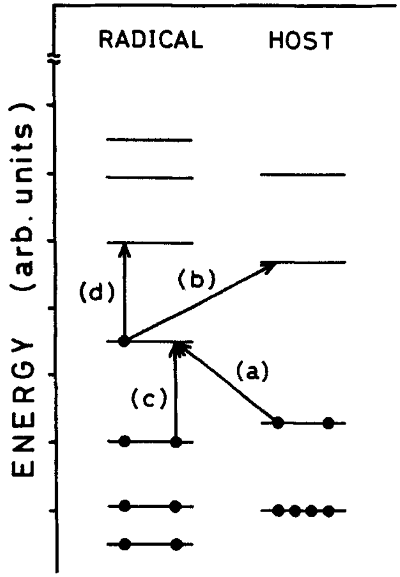
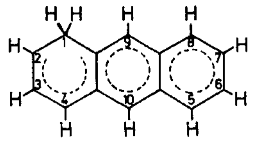


FIGURE 1 Schematic one-electron energy diagram of a pair of cyclohexadienyl-type radical and host aromatic hydrocarbon molecule. (a) and (b) represent charge transfer transitions and (c) and (d) the intra-radical transitions.

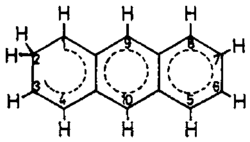
other charge transfer excited state give information of the resonance transfer integral between host molecules.[7]

In view of such interesting nature of the charge transfer transitions associated with the hydronaphthyl radical, it is of interest to extend the observation of the charge transfer transitions to other cyclohexadienyl-type radicals in crystal whose resonance transfer integrals show apparently larger values than those in naphthalene crystal. It has been shown that dibenzo-cyclohexadienyl radicals (referred to as DBCR) are produced in anthracene single crystals by ionizing radiation.[8] Three types of DBCR have been assigned: the additional hydrogen atom being attached at the positions 1, 2 and 9 as shown in Figure 2. All of these radicals are produced by irradiation at liquid nitrogen temperature, but the stability against thermal bleaching decreases in order of 9-, 1- and 2-DBCR. Thus the optical absorption lines associated with each radical could be distinguished.

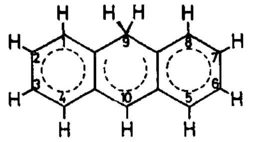
In this paper, we analyzed the optical absorption spectra of DBCR in anthracene crystal. Similarly as the hydronaphthyl radical in naphthalene single crystals, existence of radical-host charge transfer transitions for each DBCR in anthracene single crystals has been verified. The splitting and the intensity of the charge-transfer lines are discussed in some detail.



1-dibenzo-cyclohexadienyl radical



2-dibenzo-cyclohexadienyl radical



9-dibenzo-cyclohexadienyl radical

FIGURE 2 Dibenzo-cyclohexadienyl radicals.

II EXPERIMENTAL TECHNIQUES

Anthracene single crystals were grown by the Bridgeman method from reagent grade anthracene powder purified by distillation and zone-refining. Single crystal blocks were cut along the *a*–*b* cleavage plane and specimens with a dimension of about 7 × 7 × 10 mm^3 were obtained. The *a*- and *b*-axes in the *a*–*b* cleavage plane were determined by double refraction. Specimens were kept at 78 K in a cryostat and were irradiated with 2 MeV electron beams from a van de Graaff accelerator. Total radiation dose was about 10^8 R and the concentration of radicals produced was about 10^{17} cm^{-3}. Specimens were then cooled to liquid helium temperature and the absorption spectra were measured with light incident along *a*- or *c*′-axis. The light emerging from the specimen were analyzed with a Shimazu monochromator GE-100 (reciprocal dispersion: 16.6 Å/mm) with a slit width of 30 μm and recorded on Kodak spectroscopic plates 103 F and 1 N. The resolution of the absorption spectra was about 0.5 Å. A 150 W Xe-lamp was used as a light source. In order to obtain the polarized absorption spectra, incident light was polarized along the *a*-, *b*-, or *c*′-axis with polarizing film.

The optical density of the plates was traced with a microphotometer. The calibration of the wavelength was made with a low pressure mercury lamp.

III EXPERIMENTAL RESULTS

The optical absorption of a specimen of anthracene single crystal irradiated at 78 K with electron beams was measured with light incident along the *c*′-axis and polarized along the *a*- or *b*-axis or with light incident along the *a*-axis and polarized *c*′- or *b*-axis. The results are shown in Figures 3(a) and (b), where *a*, *b* and *c*′ represent the absorption spectra measured with the light polarized along the *a*-, *b*-, and *c*′-axes, respectively. Only the result for the *b*-polarization obtained with the incidence along the *c*′-axis is shown but the other result was the same. Intense absorption lines at about 535 nm (Figure 3(b)), 645 nm and 675 nm (Figure 3(a)) are beyond the linear portion of the photographic sensitivity. Another measurement with a spectrophotometer indicates that the ratios of the transition dipole moment along *a*-, *b*-, and *c*′-axis are 0.8: 1.0: 1.3 for the 535 nm line, 3.0: 1.0: 2.8 for the 645 nm line, and 1.0: 0: 1.3 for the 675 nm line.

Chong and Itoh[8] have shown that the lines at 535 nm, 645 nm, and 675 nm show different thermal annealing behaviors and by comparing them with the thermal annealing of EPR line which arise from 9- and 1-DBCR, they ascribed the 535 nm and 675 nm lines to 9- and 1-DBCR, respectively. The 645 nm line, which is produced by low temperature irradiation and is annealed at a lower temperature than other DBCR, has been ascribed to 2-DBCR. In order to distinguish various lines shown in Figure 3, a specimen which has been irradiated at 78 K was warmed to room temperature and was cooled to liquid helium temperature after being kept for 2 hours and the optical absorption spectrum was obtained. The same specimen was warmed to room temperature again and cooled down after being kept for 10 hours. Some of the optical absorption lines shown in Figure 3 were annihilated by each of the above processes. According to Chong and Itoh the decay time of the 2- and 1-DBCR at room temperature are 1 and 10 hours, respectively, and that of 9-DBCR is much longer. The lines shown in Figure 3 may be divided into three classes: namely those which decay faster than 2 hours, decay between 2 and 10 hours and are stable over 10 hours at room temperature. The lines belonging to each group were assigned to 2-, 1- and 9-DBCR in order of increasing thermal stability, and are listed in Table I, II, and III. In the tables, polarization ratio of each line are shown. It is seen that the polarization ratio of the absorption lines for each DBCR is not the same. The temperature dependence of the intensity of the major lines for each DBCR has been measured between liquid helium and liquid nitrogen temperatures and found to be independent of temperature.

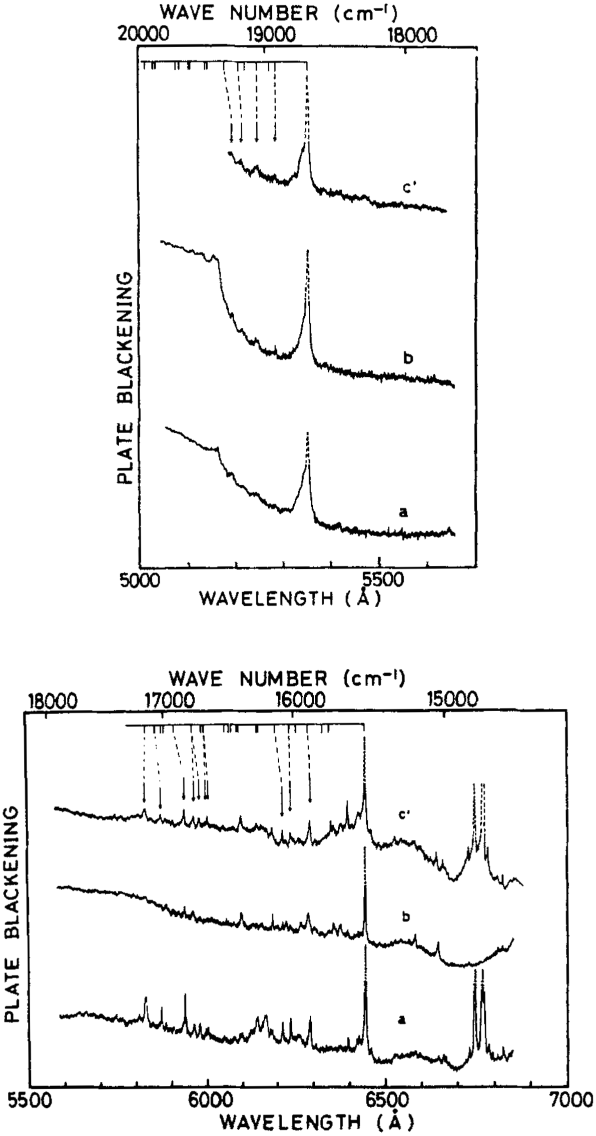


FIGURE 3 Microphotometer tracing of the absorption spectra at liquid helium temperature of anthracene crystal irradiated with electron beams at 78K (a) between 5600 Å and 7000 Å and (b) 5000 Å and 5600 Å. Curves *a*, *b* and *c*′ designate the spectra obtained with light polarized along *a*-, *b*- and *c*′-axes, respectively. The marks at the top show the position of the vibrational progression when the vibrational frequencies of the radical is assumed to be the same as those of the anthracene molecule. The arrows show the assignment of the vibrational progression.

TABLE I

Optical absorption lines of 2-DBCR

Wavelength (Å)	Wave number (cm^{-1})	Intensity[a]	Polarization ratio						Assignment
			Experiment			Expected			
			a	*b*	*c′*	*a*	*b*	*c′*	
6846.8	14605	vw	2	0	1	1	0	0	1 → 5
6816.4	14671	vw	0	1	0.8				
6742.8	14831	vw	0	0	1				
6680.1	14970	vw	1	0	1	1	0	17	1 → 6
6671.1	14990	vw	1	0	1	1	0	17	1 → 6
6664.8	15004	w	1	0	1	1	0	17	1 → 6
6650.2	15037	m	0.4	1	1	0.5	1	9	1 → 10
6650.9	15138	vw	1.5	1	2	0.5	1	9	1 → 10
6547.9	15272	vw	0.3	1	1.2	0.1	1	2	1 → 8
6489.8	15409	vw	0.5	1	0.9	0	1	0	1 → 17
6464.1	15470	w	1	0	1.3	1	0	2	1 → 2
6448.2	15508	vs	3.1	1	2.8	3.1	1	2.8	0 − 0
6434.7	15541	w	3	1	3	3.1	1	2.8	phonon
6430.3	15551	w	3	1	4	5	1	9	1 → 16
6423.4	15568	w	3	1	3	3.1	1	2.8	phenon
6399.3	15627	s	2	1	4	1	1	2	1 → 4
6360.4	15722	m	0	1	0.7	0.05	1	1	1 → 22
6295.2	15885	s	3.5	1	3	3.1	1	2.8	377 b_{3g}
6293.2	15890	s	3.5	1	3	12	1	9	1 → 25
6292.3	15892	s	0	1	0.2	0.5	1	0	1 → 19
6270.1	15949	w	0.7	1	0.5	0.03	1	0.6	1 → 20
6261.9	15970	vw	1	0	0.8	3	1	2	1 → 14
6239.6	16027	s	3	1	2.3	3.1	1	2.8	519 a_g
6228.4	16055	w	0.4	1	0.5	0.3	1	0.5	1 → 18
6218.4	16081	s	3	1	2.3	3.1	1	2.8	573 b_{2g}
6190.7	16153	w	0.5	1	1.2	1.4	1	1.3	1 → 28
6184.5	16169	vw	1	0	1	1	0	0.4	1 → 26
6077.7	16454	vw	1	1	1				
6057.5	16508	vw	1	1	1				
6006.6	16648	w	4	1	3	3.1	1	2.8	1147 − 7 a_g
6001.4	16662	w	4	1	3	3.1	1	2.8	1147 + 7 a_g
5982.5	16715	m	2.5	1	1.5	3.1	1	2.8	1229 − 22 a_g
5966.9	16759	m	2.5	1	1.5	3.1	1	2.8	1229 + 22 a_g
5941.4	16831	s	3.5	1	1.5	3.1	1	2.8	1323 a_g
5912.3	16914	vw	2	1	1.7				
5887.8	16984	vw	1.5	1	1				
5874.5	17023	s	4	1	2	3.1	1	2.8	1515 a_g
5832.1	17146	s	4	1	2	3.1	1	2.8	1643 − 5 b_{3g}
5829.0	17156	s	4	1	2	3.1	1	2.8	1643 + 5 b_{3g}

[a] The notations vs, s, m, w, and vw designate very strong, strong, medium, weak and very weak, respectively.

TABLE II

Optical absorption lines of 1-DBCR

Wavelength	Wave number		Polarization ratio						
			Experiment			Expected			
(Å)	(cm^{-1})	Intensity[a]	*a*	*b*	*c'*	*a*	*b*	*c'*	Assignment
6829.2	14643	w	3	1	2				
6810.6	14683	vw	1	0	1	1	0	0	1 → 5
6798.3	14710	vw	1	0	0.6	1	0	0	1 → 5
6787.8	14732	m	1	0	2	1	0	17	1 → 6
6776.1	14758	vs	1	0	1.3	1	0	17	1 → 6
6770.0	14771	vs	1	0	1.3	1	0	17	1 → 6
6750.2	14814	vs	1	0	1.3	1	0	17	1 → 6
6734.6	14849	m	1	0	1.3	1	0	17	1 → 6
6588.2	15179	w	0.5	1	0.7	0.2	1	0	1 → 21
6533.7	15305	w	1.2	1	1.3	2	1	0	1 → 7
6382.4	15668	m	0.4	1	0.7	0.1	1	2	1 → 8
6377.3	15681	m	0.4	1	0.7	0.1	1	2	1 → 8
6368.3	15703	w	0.4	1	0.7	0.1	1	2	1 → 8
6353.8	15739	w	0.2	1	5	5	1	9	1 → 16
6347.0	15755	vw	0	1	0	0	1	0	1 → 17
6329.1	15800	vw	0	1	0.7	0.05	1	1	1 → 22
6308.4	15852	vw	0.2	1	0.7	1	1	2	1 → 4
6170.1	16207	s	9	1	3.5	12	1	9	1 → 25
6166.3	16217	s	9	1	3.5	12	1	9	1 → 25
6158.6	16237	w	0.8	1	1	0.5	1	1	1 → 24
6150.0	16260	s	9	1	3.5	12	1	9	1 → 25
6132.5	16307	w	0.8	1	1	0.03	1	0.6	1 → 20
6128.4	16317	w	0.8	1	1	0.03	1	0.6	1 → 20
6102.8	16386	m	0.4	1	1	0.3	1	0.5	1 → 18
6101.0	16391	m	0.4	1	1	0.3	1	0.5	1 → 18

[a] The notations vs, s, m, w and vw designate very strong, strong, medium, weak and very weak, respectively.

IV DISCUSSION

1 Assignment of lines for 9- and 2-DBCR

The optical absorption lines associated with 9- and 2-DBCR were assigned similarly as those for 1- and 2-hydronaphthyl radicals in naphthalene crystal. Among the lines listed in Tables I and III, there are considerable number of lines which has the same polarization as the most intense lines for 9-DBCR at 5353 Å and for 2-DBCR at 6448 Å. Among these lines the most intense lines for each DBCR may be ascribed to the intra-radical transition uncoupled with vibrational quanta namely, 0–0 vibrational line. On the other

TABLE III

Optical absorption of a 9-DBCR

Wavelength (Å)	Wave number (cm^{-1})	Intensity[a]	Polarization ratio						Assignment
			Experiment			Expected			
			a	*b*	*c′*	*a*	*b*	*c′*	
5643.5	17720	vw	4	1	1	1	0	0	1 → 5
5390.4	18551	vw	0	1	2	0.5	1	9	1 → 10
5364.1	18642	vw	1.5	1	2	1	0	17	1 → 6
5352.6	18682	vs	0.8	1	1.3	0.8	1	1.3	0 – 0
5343.1	18716	w	1	1	1.2	0.8	0	1.3	phonon
5330.1	18761	w	1	0	0.8	1	0	2.1	1 → 2
5323.0	18786	vw	0	1	1	0.1	1	2.3	1 → 8
5303.2	18857	vw	2	1	1	5	1	9	1 → 16
5287.9	18911	w	0.8	1	1.5	0.8	1	1.3	229 b_{2g}
5246.9	19059	w	0	1	1	0.05	1	1	1 → 22
5243.4	19072	w	1	1	1	0.8	1	1.3	390 b_{3g}
5220.3	19156	vw	1.5	1	0.8	18	1	0	1 → 15
5212.1	19186	w	1	1	1	0.8	1	3	504 a_g
5192.7	19258	w	1	1	1	0.8	1	3	622 b_{2g}
5182.5	19296	vw	0.5	1	1	0.5	1	1	1 → 24
5161.5	19374	w	1	1		0.5	1	0	1 → 19
5154.6	19400	w	0	1		0.03	1	0.6	1 → 20
5130.3	19492	w	0	1		0.3	1	0.5	1 → 18

[a] The notations vs, s, m, w and vw designate very strong, strong, medium, weak and very weak, respectively.

hand the lines around 6292 Å for 2-DBCR, for example, have no a-component. Such an orientation of the transition dipole can not be attained in the oriented gas model and therefore this line can not be ascribed to an intra-radical transition. Thus only the lines which have the same direction of transition dipole moment as the 0–0 vibrational lines and are separated from the 0–0 line by vibrational frequencies of anthracene molecule were ascribed to the vibrational progression as shown by arrows at the top of Figure 3. The assignment of the vibrational lines are shown in Table I and III, where the irreducible representation of the anthracene vibrational modes which have nearly the same energy as the DBCR vibrational modes are shown. The slight difference between the obtained vibrational energies of DBCR and of anthracene molecule may be ascribed to the effect of the addition of a hydrogen atom. Similarly as the case of the hydronaphthyl radicals in naphthalene crystals each remaining line was ascribed to a charge transfer transition from DBCR to each anthracene molecule around the radical. Refering to Figure 4, the radical is supposed to be located at position 1 and molecules are numbered as indicated. The assignment of the charge

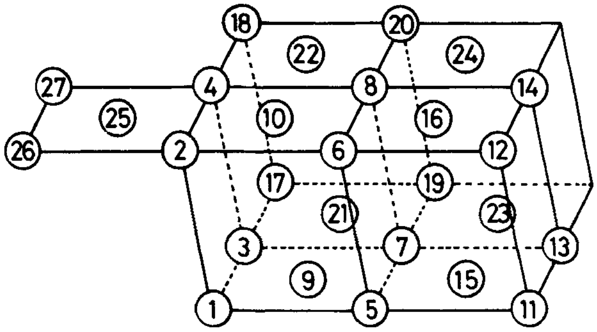


FIGURE 4 Schematic diagram of the lattice of anthracene single crystals showing numbering of the molecular sites, the radical being situated at position 1.

transfer transition was made on the following basis:

1) The charge transfer transition to a nearer molecule shows a smaller transition energy.

2) Each charge transfer transition has the same polarization as the charge transfer direction.

The results of the assignment are shown in Table I and III for 2- and 9-DBCR, respectively.

The relation between transition energy E and charge transfer distance r is plotted by open circles in Figure 5(a) and (b) for 2- and 9-DBCR, respectively. The solid line indicates the best fit curve to Eq. (1) with $\varepsilon = 3.46$. E_∞ has been determined to be 18300 cm^{-1} and 21730 cm^{-1} for 2- and 9-DBCR, respectively. It is clear that the charge transfer energy depends on the distance as shown by Eq. (1) and this fact verifies that these lines are indeed originated from charge transfer transitions between the radical and the host molecule. In some cases a few lines were ascribed to the same charge transfer states and they are considered to be due to the splitting of the charge transfer lines to nearly equivalent sites, on which description is made later.

2 Assignment of lines for 1-DBCR

The most intense line for 1-DBCR around 675 nm has no *b*-component and cannot be ascribed to the intra-radical transition. Any progressional series of lines with the same polarization as the most intense line, as observed for 9- and 2-DBCR, cannot be found in the absorption lines for 1-DBCR. Therefore any lines for 1-DBCR cannot be ascribed to the intra-radical transition nor its vibrational progression. Moreover, the absence of the

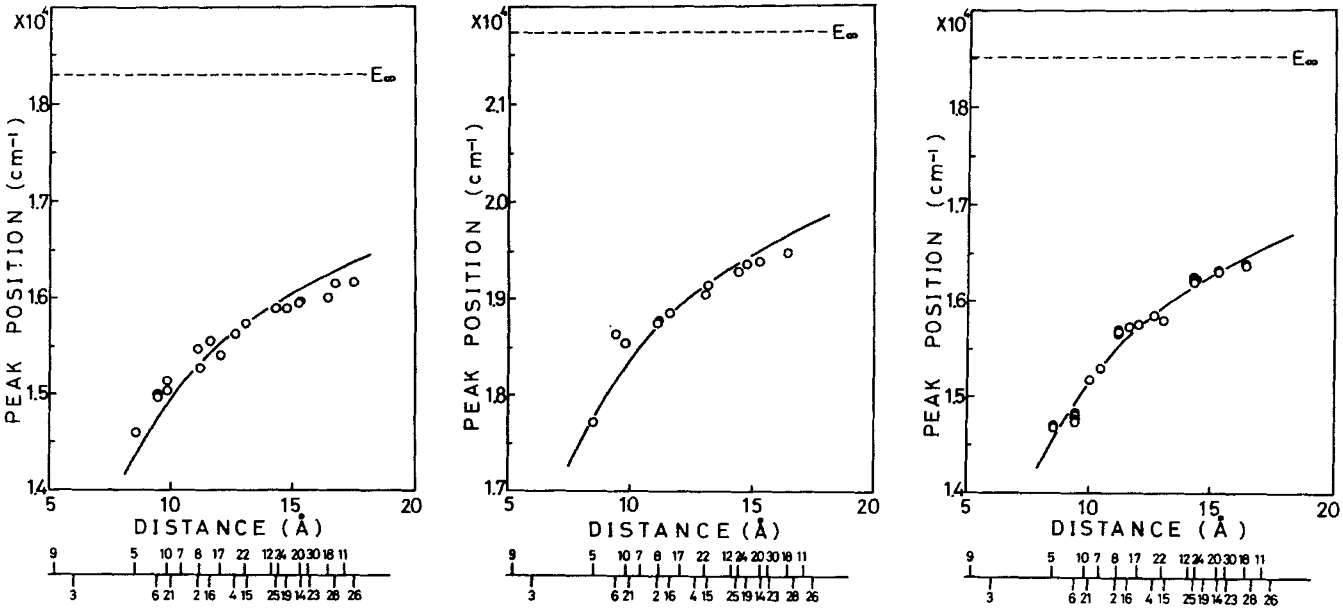


FIGURE 5 Relation between the charge transfer energy and the distance of the charge transfer (a) for 2-dibenzo-cyclohexadienyl radical, (b) for 9-dibenzo-cyclohexadienyl radical and (c) for 1-dibenzo-cyclohexadienyl radical. The numbers at the bottom of the figure shows the molecular number indicated in Figure 4.

temperature dependence of the lines exclude the possibility that the observed lines are vibronic.

A significant difference between the absorption lines for 1-DBCR and other lines is that a few groups of aggregated lines with the same polarization are observed for 1-DBCR. Each group of lines was tentatively assigned to a charge transfer transition to each molecule around the radical. The result of the assignment is shown in Table II. The relation between transition energy E and charge transfer distance r is shown in Figure 5(c) by open circles. E_∞ has been determined to be 18510 cm^{-1} from the best fit curve to Eq. (1) with $\varepsilon = 3.46$, which is shown by a solid line. The experimental relation is in accordance with Eq. (1), verifying that these lines are originated from the charge transfer transitions between the radical and the host molecules. It is of interest to note that charge transfer transitions are much more intense than intra-radical transitions for 1-DBCR. This problem is discussed later.

3 Splitting of the charge transfer lines

The splitting of the charge transfer lines from 1-hydronaphthyl radical to the naphthalene molecule at positions 10, 16 and 25 has been observed and ascribed to the splitting of the charge transfer excited state due to the finite transfer resonance interaction between two neighboring equivalent molecules which are at equal distance from the radical.[7] No splitting was observed for other charge transfer transitions. For anthracene single crystals, splitting has been observed for the several charge transfer lines, namely transitions 1 → 6, 1 → 10 for 2-DBCR and 1 → 5, 1 → 6, 1 → 8, 1 → 25, 1 → 20 and 1 → 18 for 1-DBCR. Each of the molecules to which the transition 1 → 10 and 1 → 25 occur has a directly interacting equivalent molecule and the splitting due to the mechanism discussed above is expected to occur. As seen from Tables I, II and III the splitting appear in the other charge transfer transitions and in some cases more than two lines are observed for anthracene.

The site splitting, is expected to be larger in 1- and 2-DBCR than in hydronaphthyl radicals and in 9-DBCR. The splitting of the lines 1 → 5, 1 → 20 and 1 → 18 may be ascribed to the site splitting, of which magnitudes are 27 cm^{-1}, 10 cm^{-1}, and 5 cm^{-1}, respectively, and are decreasing as the distance of transition increases. Similarly the smaller splitting, 10 cm^{-1}, of the 1 → 25 transition may be ascribed to the site splitting. It follows that the larger splitting 48 cm^{-1} is mainly due to the resonance transfer interaction between two equivalent molecules. According to the calculation by Katz *et al.*[9] the value of the resonance transfer integral to this direction is 54.07 cm^{-1} for electrons and 90.22 cm^{-1} for holes and such larger splitting should occur.

The presence of more than two lines for the 1 → 6 and 1 → 8 transitions requires further consideration. A calculation of the charge transfer distance indicates that each of the molecules 6 and 8 has a nearest neighbor, 10 and 16, respectively, almost equally separated from the radical. The difference between the coulomb potential from the radical to molecules 6 and 10 is 159 cm^{-1} and that between 8 and 16 is 111 cm^{-1}. Theoretical calculation by Katz *et al.*[8] indicates that the resonance transfer integral between these neighboring molecules are 93.21 cm^{-1} for electrons and 68.92 cm^{-1} for holes. Thus the resonance interaction may cause mixing of the charge transfer excited states. Therefore, the aggregate lines ascribed to 1 → 6 and 1 → 8 transitions for 1-DBCR are expected to arise from the transitions to the mixed charge transfer excited state with molecules 10 and 16, respectively. The splitting into five lines for the 1 → 6 transition can be explained by considering the resonant interaction with 1 → 10 transition and the site splitting of the 1 → 6 and 1 → 10 transitions. In this case the magnitude of the splitting represent neither the resonance transfer integral nor the site splitting: a similar result was observed for naphthalene, in which case the resonant splitting was reduced due to the configuration interaction between molecules 6 and 10. Similar arguments could be made for the 1 → 8 transition for 1-DBCR and 1 → 6 transition for 2-DBCR. The fact that the direction of the transition dipole moment are oriented along 1 → 6 direction, in spite of the interaction with 1 → 10 transition is discussed in the next section. The assignment shown in Table I and II are made according to the polarization of the transitions but the final state of the charge transfer transition may be mixed with other molecular orbitals.

4 Intensity of charge transfer transitions

The oscillator strength of the 0–0 vibrational line of 1-hydronaphthyl radical has been determined by Chong *et al.*[10] to be 10^{-3}. Although the accurate determination of the oscillator strength of DBCR has not yet been made, the values for the 9- and 2-DBCR may not differ too much from that of 1-hydronaphthyl radical. The intensity of the strongest charge transfer transitions from the 9- and 2-DBCR is smaller than that of the intra-radical 0–0 transition by two orders of magnitude. Therefore it is expected that the oscillator strength of the charge transfer transitions for 9-DBCR and 2-DBCR may be of the order of 10^{-5}. In view of the EPR works,[8] the oscillator strength of the strongest charge transfer transitions for 1-DBCR, in which no intra-radical transition was observed, was estimated to be nearly of the same order of magnitude as that for the intra-radical transition of 9-DBCR: about 10^{-3}. The origin of the dipole moment of the charge transfer transition is discussed in some detail.

The ground state Ψ_g of the radical wave function may be assumed to be isolated in view of that it is energetically separated from other levels. The charge transfer excited state Φ, an ionized radical and an anthracene ion, may be mixed with the radical excited state Ψ_e: $\Phi + c_1\Psi_e$. The coefficient c_1, whose absolute value is much smaller than 1, may be given by

$$c_1 = \frac{\langle\Psi_e|H|\Phi\rangle}{E_a - E_e},$$

where E_a and E_e are the energy of the charge transfer state and of the radical excited state, respectively. H is the Hamiltonian of the host crystal including a radical and has approximately the C_{2h} symmetry. Φ may be a linear combination of the wave functions of the charge transfer state to molecules situated at equivalent positions and roughly belongs one of the irreducible representation of the C_{2h} group. The transition dipole moment may arise either from $\langle\Phi|\mu|\Psi_g\rangle$ or $c_1\langle\Psi_e|\mu|\Psi_g\rangle$. The absence of the strong dependence of the intensity of the charge transfer lines on the distance r may exclude the possibility that the former makes an important contribution. Instead of that it is observed that the intensity of the charge transfer lines situated energerically in the proximity of strong vibrational lines is relatively large. It follows that the intra-radical transition dipoles $\langle\Psi_e|\mu|\Psi_g\rangle$ including those to the vibrational state make a large contribution in the charge transfer transition. Lack of symmetry in DBCR may make the transition dipole moment of the charge transfer transition to various directions around the radical finite.

Refering to Figure 1, the small oscillator strength of the intraradical transition has been shown to arise from the cancellation of the dipole moment of the transition (c) from the highest occupied level to the half-occupied level and the transition (d) from the half-occupied level to the lowest unoccupied level by a molecular orbital calculation. The mixed states of the charge transfer state with the radical excited state may be expressed as $\Phi + \alpha_1\chi_c + \alpha_2\chi_d$, the coefficients α_1 and α_2 are correlated with the resonance transfer integral between each of the radical excited states and the charge transfer state and may not be necessarily the same. Moreover the transition dipoles from the ground state to either of the radical excited state is relatively large as described above. Thus if either of α_1 or α_2 have a value of 10^{-2}, then the observed intensity of the charge transfer transitions for 9- and 2-DBCR can be accounted for. Since the strongest charge transfer lines are accompanied with the vibrational lines separated less than 10^{-3} eV, as in the case of the transitions 1 → 4, 1 → 25 and 1 → 19 in 2-DBCR and 1 → 2 and 1 → 22 in 9-DBCR, even the transfer integral of 10^{-5} eV would explain the observed oscillator strength of the charge transfer transition. Such amount of the resonance transfer interaction is not unexpected, for the charge transfer transitions in same unit cell. The apparent large oscillator strength of the charge transfer transition for 1-DBCR may be due to an accidental degeneracy of the charge transfer and the radical excited states.

The other significant feature of the charge transfer transitions for 1-DBCR is that the direction of the transition dipole 1 → 6 does not have any *b*-component although the observed level splitting cannot be explained without considering the mixing with the transition 1 → 10. This is only the exceptional case, in which the polarization of the absorption lines does not represent the direction of the charge transfer. One may assume that the resonance interaction between carbon $2p\pi$ orbitals in 1-DBCR and those in the molecule 10 is accidentally close to zero, and the transition dipole moment towards the direction 1 → 10 is exceptionally small. Understanding of such behaviors on the charge transfer transition may be accomplished by a detailed molecular orbital calculation and may give a critical check of the electronic interaction between the host molecule and the radical which is known to be properly oriented in the lattice.[11]

V Conclusion

The charge transfer transitions from 1-, 2-, and 9-DBCR to the anthracene molecules separated by various distance from the radicals were identified. The relation between the transition energy and the transfer distance was found to follow a coulombic relation as obtained for the similar radicals in naphthalene crystals. The splitting of the charge transfer lines was observed and ascribed to the resonance interaction between equivalent molecules and to the site symmetry. The charge transfer lines for 1-DBCR were found to be much stronger than the intra-radical lines of 1-DBCR. This result was explained in view of that the charge transfer transitions are the admixture of the electron and hole transitions which borrow the intensities from two intra-radical transitions in a different amount, destroying the cancellation of the transition dipoles of the two intra-radical transitions.

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