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Zeeman Absorption Spectra of 2,3-Dichloro-9,10-anthraquinone Crystals

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Polarized $T \leftarrow S_0$ absorption spectra were measured for 2,3-dichloro-9,10-anthraquinone melt-grown single crystals in a magnetic field of 50 kOe. From the analysis of the Zeeman absorption patterns, the lowest triplet state of 2,3-dichloro-9,10-anthraquinone in the crystalline state has been assigned to $^3A_1(\pi\pi^*)$. The c-polarized first absorption peak at 21734.7 cm^{-1} has been interpreted as gaining intensity mainly from an x-polarized transition from the ground state to a $B_1(n\pi^*)$ perturbing singlet state, which is directly spin-orbit-coupled with the y spin-sublevel of the $^3A_1$ state. The a- and b-polarized first peaks, at 21733.9 and 21733.6 cm^{-1}, respectively, have been interpreted as gaining intensity through the configurational mixing of the $^3A_1(\pi\pi^*)$ state with a nearby $^3B_1(n\pi^*)$ state.

Recently, we have studied the triplet states of 9,10-anthraquinone (abbreviated to AQ) crystals by Zeeman absorption spectroscopy,[1] and assigned the origin peak of the lowest triplet state at 22154.0 cm^{-1} to $^3B_{1g}$ $(n\pi^*)$. The phosphorescence spectrum of an AQ crystal was also indicative of an $n\pi^*$ emitting state, the strongest peak being located 1680 cm^{-1} from the origin peak of the phosphorescence. We have extended our study to 2,3-dichloro-9,10-anthraquinone (abbreviated to 2,3-DCAQ) in order to determine whether the compound, a substituted AQ, also possesses the lowest triplet state of $n\pi^*$ character.

We chose 2,3-DCAQ because it crystallizes in such a manner that its molecular x, y, and z axes are nearly parallel to the crystallographic c, b, and a axes, respectively.[2] This kind of molecular alignment in a crystal is favorable for determining the direction of the electronic transition moment. We will present an assignment of the triplet-state electronic configuration of 2,3-DCAQ crystals, based on experimental proof obtained by means of Zeeman spectroscopy.

Experimental

2,3-DCAQ was prepared by cyclocondensation of *o*-(3,4-dichlorobenzoyl)benzoic acid obtained by the Friedel-Crafts reaction between *o*-dichlorobenzene and phthalic anhydride.[3] Crude 2,3-DCAQ was purified by recrystallization twice from benzene, sublimation *in vacuo*, and then by zone-refining carried out for 150 passes, three successive refinings of 50 passes each. A single crystal was melt-grown in a Bridgman furnace. Crystal samples of suitable size, *ca.* 5×5 mm^2 in area and 2—5 mm in thickness, were cut from the crystal, and their faces identified by the X-ray diffraction method.

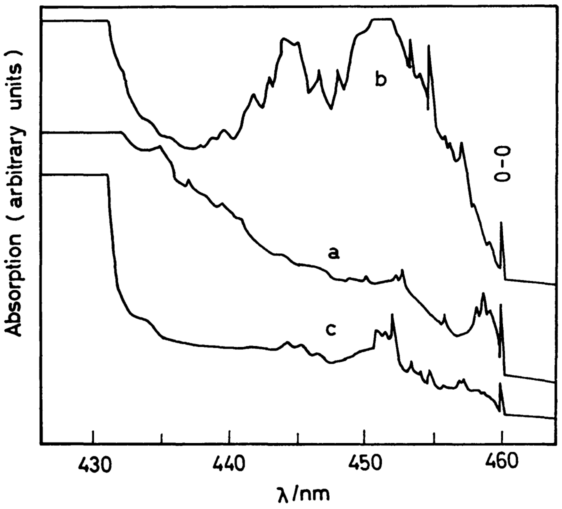

Fig. 1. Polarized absorption spectra of 2,3-DCAQ crystals at 1.7 K. (a) E//a, (b) E//b, (c) E//c.

Absorption spectra were analyzed with an NLM-E2M spectrometer equipped with an Echelles grating in a Czerny-Turner mount. The reciprocal dispersion of the spectrometer was 0.055 nm mm^{-1} at 460 nm in the 12 th order of the grating. The incident light from an Osram 450 W regulated xenon-arc-lamp was chopped at 720 Hz, the light passing through the sample being detected by a combination of an HTV R376 photomultiplier tube and an NF LI-572 lock-in amplifier.

Two types of optical cryostats including superconducting magnets, an Oxford 55 and a Sinkukiko 60, were used for Zeeman spectroscopy. The incident light propagates along the magnetic field in the former and passes through the sample perpendicular to the magnetic field in the latter. The magnetic field could be controlled to any required value up to *ca.* 55 kOe[†]. Phosphoresence of a crystal immersed in pumped liquid helium was excited by 365 nm radiation filtered from an ORC 1 kW superhigh-pressure mercury arc through Toshiba UV-D1C and IRQ-80 filters.

Results and Discussion

Figure 1 shows the polarized absorption spectra of 2,3-DCAQ crystals at 1.7 K. The recordings of spectra (a) and (b) refer to a 3.8 mm thick crystal with light incident on the ab plane; the recording of (c) refers to a 2.3 mm crystal with light incident on the ac plane. The first peak, moderately intense and sharp (*ca.* 1.5 cm^{-1} in width) was observed at approximately 460 nm. Several successive intense peaks were observed in the spectral region 460—440 nm. All the peaks were found to split into sublines upon the application of a magnetic field, which indicates that they could be ascribed to the $T \leftarrow S_0$ transitions.

The high-resolution spectrometer revealed that the a- and the b-polarized first peaks were located at 21733.9 and 21733.6 cm^{-1} (A=0.87 for a 3.8 mm thick crystal), respectively, and the c-polarized first peak at 21734.7 cm^{-1}. The wave-number difference of *ca.* 1 cm^{-1} observed between the c-polarized peak and the a- or b-polarized peak is understood as an indication of the triplet factor group splitting.

[†] $Oe = 1000/4\pi$ A m^{-1}.

The phosphorescence spectrum observed for a 2,3-DCAQ crystal at 1.7 K shows sharp and intense peaks at 460.4 nm (21712 cm^{-1}) and 499.0 nm (20033 cm^{-1}) (Fig. 2), the former located *ca.* 22 cm^{-1} below the first peak in the absorption spectrum, and the latter 1679 cm^{-1} from the former peak. The wave-number difference corresponds to the C=O stretching mode frequency of 1676 cm^{-1} observed for AQ in the IR spectrum.[4] A moderately intense peak was observed at 543.5 nm (18393 cm^{-1}), which could be assigned to the overtone frequency of the C=O stretching mode.

The phosphorescence spectrum of 2,3-DCAQ in heptane (Shpol'skii matrix) at 1.7 K, on the other hand, shows a weak peak at 457.6 nm (21844 cm^{-1}) and a sharp, strongest peak at 495.9 nm (20157 cm^{-1}), located 1687 cm^{-1} from the weak peak (Fig. 3). Each peak is accompanied by two other peaks at intervals of 66 and 29 cm^{-1}. The peaks seem to arise from molecules in different sites in the matrix. A similar multiple structure has been reported for AQ in heptane.[5]

From the results, the first peaks in the absorption spectra are considered to arise from the origin for the lowest $T_1 \leftarrow S_0$ transition of 2,3-DCAQ.

The crystal structure of 2,3-DCAQ corresponds to a space group symmetry of D_2 with four molecules per unit cell. The molecules can be regarded as planar in the crystal, belonging to the C_{2v} point group.[2] The z axis is taken along the molecular twofold axis, and the z,y-plane as the plane of the molecule. Table 1 gives the squared direction cosines of the molecular axes with respect to the crystallographic axes. The x, y, and z molecular axes are nearly parallel to the c, b, and a crystallographic axes, respectively.

Figure 4 shows the Zeeman patterns for the first absorption peaks observed with polarized light, E, in the presence of a magnetic field, *H*, of 50 kOe, directed along the a, b, and c crystallographic axes of the 2,3-DCAQ single crystal. A single peak was found to split into sublines in the magnetic field. The transition to a triplet state from the ground state acquires the polarization of the transition to a perturbing singlet state, and assumes a spin-orbit interaction between the perturbing singlet state and the triplet state in the first-order approximation. The intensities of the individual Zeeman sublines depend on the polarization of the transition to the perturbing singlet state, p, and the route effective in the spin-orbit interaction, u. The relative intensities of the Zeeman sublines for

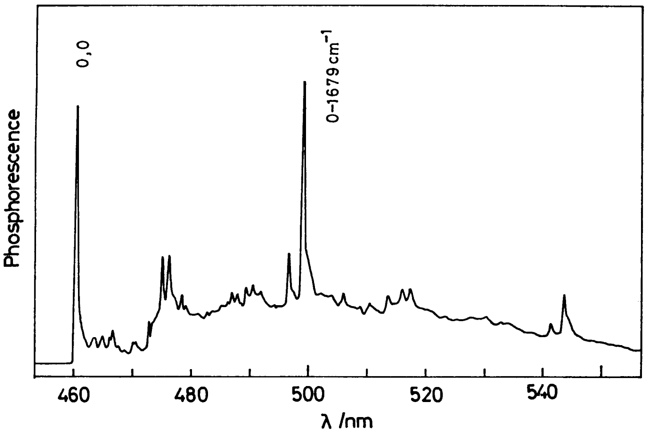

Fig. 2. Phosphorescence spectrum of a 2,3-DCAQ crystal at 1.7 K.

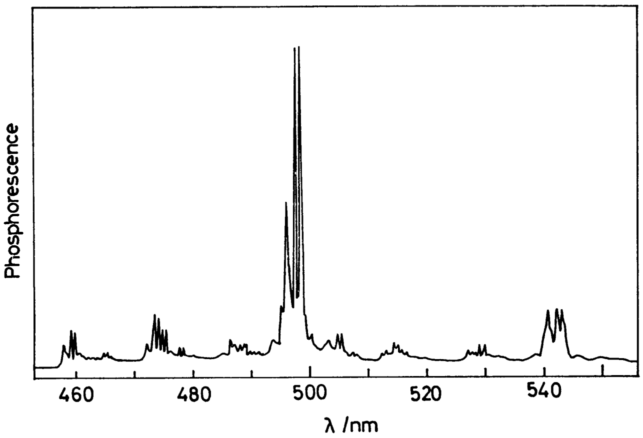

Fig. 3. Phosphorescence spectrum of 2,3-DCAQ in heptane at 1.7 K.

TABLE 1. SQUARED DIRECTION COSINES FOR A 2,3-DCAO CRYSTAL

	x	y	z
a	0.082	0.001	0.917
b	0.075	0.923	0.002
c	0.843	0.077	0.080

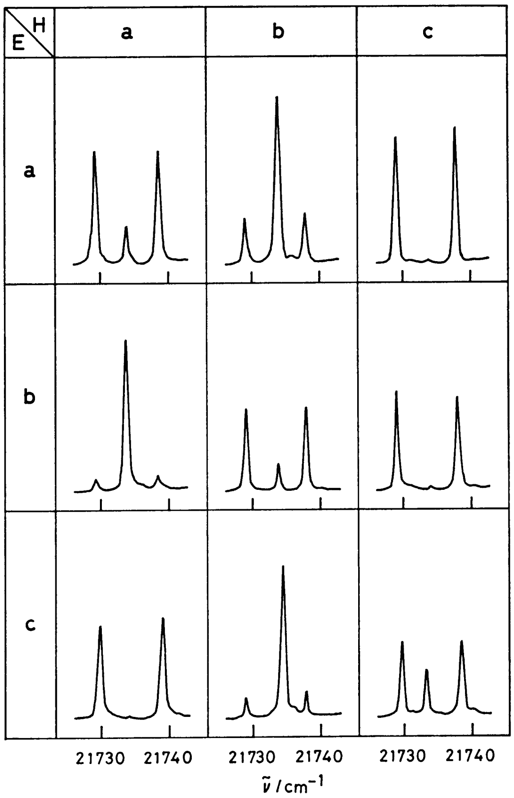

Fig. 4. Zeeman patterns of the first absorption peaks for 2,3-DCAQ crystals at 50 kOe.

TABLE 2. RELATIVE INTENSITIES OF THE ZEEMAN SUBLINES FOR A TRIPLET FACTOR GROUP OF D_2 SYMMETRY

H	E	A I_0	A $I_{\pm 1}$	B_1 I_0	B_1 $I_{\pm 1}$	B_2 I_0	B_2 $I_{\pm 1}$	B_3 I_0	B_3 $I_{\pm 1}$
a	a	$2l_u^2l_p^2$					$n_u^2l_p^2$		$m_u^2l_p^2$
	b		$m_u^2m_p^2$		$n_u^2m_p^2$			$2l_u^2m_p^2$	
	c		$n_u^2n_p^2$		$m_u^2n_p^2$	$2l_u^2n_p^2$			
b	a		$l_u^2l_p^2$				$n_u^2l_p^2$	$2m_u^2l_p^2$	
	b	$2m_u^2m_p^2$			$n_u^2m_p^2$				$l_u^2m_p^2$
	c		$n_u^2n_p^2$	$2m_u^2n_p^2$			$l_u^2n_p^2$		
c	a		$l_u^2l_p^2$			$2n_u^2l_p^2$			$m_u^2l_p^2$
	b		$m_u^2m_p^2$	$2n_u^2m_p^2$					$l_u^2m_p^2$
	c	$2n_u^2n_p^2$			$m_u^2n_p^2$		$l_u^2n_p^2$		

TABLE 3. INTENSITY RATIOS, $I_0/I_{\pm 1}$, CALCULATED FOR X-, Y-, AND Z-ROUTES IN THE SPIN-ORBIT INTERACTION FOR 2,3-DCAO

H	u x	u y	u z
a	0.18	0.00	22.2
b	0.16	23.9	0.01
c	10.8	0.17	0.17

a triplet factor group of D_2 symmetry, obtained on the assumption that only one of the spin-orbit-coupling routes is effective,[6] are summarized in Table 2, where l_p, m_p, and n_p (also l_u, m_u, and n_u) represent the direction cosines of the axes a, b, and c with respect to the molecular axis p (also u), respectively, and I_0 and $I_{\pm 1}$ represent the relative intensity of the central Zeeman line and that of the wing lines, respectively.

In the absence of a magnetic field, the absorption intensities observed with the a-, b-, and c-polarized lights, I_a, I_b, and I_c, are given as $2l_p^2$, $2m_p^2$, and $2n_p^2$, respectively, which are seen to be independent of the effective route in the spin-orbit interaction. The intensity ratios, $I_a : I_b : I_c$, are calculated to be 0.1 : 0.09 : 1 for an x-polarized transition in the molecular framework, showing that such a transition provides its intensity predominantly to the c-polarized absorption. The ratios are similarly calculated to be 0 : 1 : 0.08 for a y-polarized transition, and 1 : 0 : 0.09 for a z-polarized transition. However, the absorptions for the 2,3-DCAQ crystal were observed along all three crystallographic axes, and the ratios, $I_0 : I_b : I_c$, were found to be 1 : 0.6 : 0.4. This indicates that not only a z-polarized transition but also y- and x-polarized transitions are included in the absorption.

Table 2 gives the intensity ratio, $I_0/I_{\pm 1}$, for each direction of a magnetic field. The ratios are equal to $2l_u^2/(1-l_u^2)$, $2m_u^2/(1-m_u^2)$, and $2n_u^2/(1-n_u^2)$ for a magnetic field directed along the a-, b-, and c-axes, respectively, which are seen to be independent of the polarization of the transition in the molecule. Ratios calculated for x-, y-, and z-routes in the spin-orbit interaction are given in Table 3.

As shown in Fig. 4, the Zeeman pattern such that the central line is stronger than the wing lines is observed only in a b-directed magnetic field for the c-polarized peak, in an a-directed field for the b-polarized peak, and in a b-directed field for the a-polarized peak. This indicates that each peak gains intensity through only one route in the spin-orbit interaction. The Zeeman pattern with a strong central line appears in a b-directed magnetic field for the y route, and in an a-directed field for the z route (Table 3).

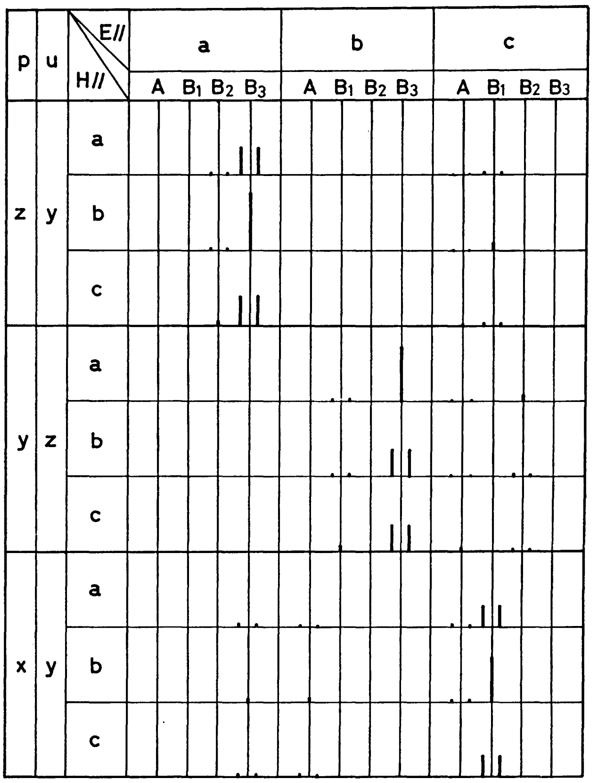

Fig. 5. Calculated relative intensities of the Zeeman sublines for a 2,3-DCAQ crystal.

The c-polarized peak, which arises mainly from an x-polarized transition in the molecular framework, shows the Zeeman pattern with a strong central line in a b-directed magnetic field. Thus an x-polarized transition to a perturbing singlet state is considered to provide intensity through the y route to the transition to the triplet state of A_1 species. Similarly, the Zeeman patterns for the b- and a-polarized peaks show that y- and z-polarized transitions also provide intensity to the absorption to the lowest triplet state through the z and y routes, respectively.

The intensities of the Zeeman sublines, I_0 and $I_{\pm 1}$, for each triplet factor group state of a 2,3-DCAQ crystal are calculated from Tables 1 and 2 for these three combinations of polarization, p, and spin-orbit-coupling route, u. Figure 5 shows the relative values of the intensities in thick bars. It is seen that the a- and b-polarized absorptions arise mainly from the transition to the B_3 factor group state, and the c-polarized absorption mainly from the transition to the B_1 state. This seems to explain the wave-number difference of *ca.* 1 cm^{-1} observed between the c- and the a- or b-polarized first absorption peaks, *i.e.*, the triplet factor group splitting.

A simple molecular-orbital description of 2,3-DCAQ leads to the prediction that the low-energy $\pi\pi^*$ state is of species A_1 or B_2, and the $n\pi^*$ state is of species A_2 or B_1. In general, the transition to an $n\pi^*$ triplet state is much stronger, 10^2—10^3 times, than that to a $\pi\pi^*$ triplet state. Thus if the $\pi\pi^*$ triplet state is mixed more than 10% with the triplet state of $n\pi^*$ character, the general appearance of the spectrum and the polarization characteristics are expected to resemble those of pure $^3n\pi^*$ state.[7]

The absorption to the lowest triplet state of the 2,3-DCAQ crystal was found to have a mixed character of the $^3\pi\pi^*$ and $^3n\pi^*$ states, as shown by the direction of its polarization. It is therefore concluded that the lowest triplet state belongs to $^3A_1(\pi\pi^*)$, gaining $n\pi^*$ character from a nearby-located $n\pi^*$ triplet state. The location of the $n\pi^*$ state could not be determined precisely, but a broad and intense b-polarized absorption arising mainly from the y-polarized transition in the molecular framework was observed at approximately 452 nm, though the maximum absorption was off-scale. The lowest $n\pi^*$ triplet state may be located in this spectral region, *ca.* 400 cm^{-1} above the lowest $\pi\pi^*$ triplet state.

For the 0—0 transition to the $^3A_1(\pi\pi^*)$ state, the possible mechanisms[8] for gaining the major part of the intensity are (i) direct spin-orbit coupling between the $^3A_1$ state and an $n\pi^*$ perturbing singlet state, (ii) configurational mixing between the $^3A_1$ state and a nearby $n\pi^*$ triplet state,[7] and (iii) mixing of the $^3A_1$ state with a nearby $n\pi^*$ triplet state through spin-orbit interaction.[9] The observed c-polarized $T_1 \leftarrow S_0$ absorption can be explained in terms of mechanism (i): The transition to the $^3A_1(\pi\pi^*)$ state gains its intensity from an x-polarized transition to a $B_1(n\pi^*)$ perturbing singlet state through the y route in the spin orbit interaction.

We must further explain the contribution of the y route associated with the z polarization and that of the z route associated with the y polarization to the $T_1 \leftarrow S_0$ absorption. Mechanism (ii) can explain these contributions: The y and z spin-sublevels of the $^3A_1(\pi\pi^*)$ state are mixed electrostatically with the y and z spin-sublevels of a nearby $^3B_1(n\pi^*)$ state, respectively, which are in turn spin-orbit-coupled to $A_1(\pi\pi^*)$ and $B_2(\pi\pi^*)$ perturbing singlet states, respectively. The transitions from the ground state to these singlet states are expected to be z- and y-polarized, respectively. This is what we have observed for the 2,3-DCAQ crystal. Mechanism (iii) can not explain the observed z-polarized absorption from a group-theoretical point of view.

The $^3A_1(\pi\pi^*)$ state can be mixed with the other $n\pi^*$ triplet state, *i.e.*, $^3A_2(n\pi^*)$ by mechanisms (ii) and (iii). However, this scheme can not explain the observed polarization characteristics.

For a 2,3-DCAQ crystal, the absorption to the lowest triplet state of $A_1(\pi\pi^*)$ species can be explained by a mechanism in which direct spin-orbit coupling with a perturbing $^1B_1(n\pi^*)$ state and electrostatic mixing with a nearby $^3B_1(n\pi^*)$ state operate for the $^3A_1(\pi\pi^*)$ state simultaneously.

The phosphorescence spectrum of 2,3-DCAQ in heptane showed a weak origin peak and a strongest peak corresponding to the C=O stretching mode. The same features were observed in the phosphorescence spectra of 1-chloro-AQ and 2-chloro-AQ in heptane at 1.7 K. The spectra are indicative of an $n\pi^*$ emitting state. If the emitting state is regarded as the T_1 state for 2,3-DCAQ in heptane, a comparison between the heptane-solution spectrum and the crystal spectrum shows that a low-lying $^3\pi\pi^*$ state is lowered in energy below the $^3n\pi^*$ state by changing the environment from heptane to 2,3-DCAQ. The phosphorescence spectra of aromatic carbonyl compounds, where the $n\pi^*$ and $\pi\pi^*$ triplet states are very close to each other, have been reported to be strikingly dependent on the nature of the environment.[10–13]

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