

# Circular Dichroism Spectra of Anion Radical and Dianion of 2,2'-Dimethyl-1,1'-bianthryl

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**Abstract:** The circular dichroism (CD) spectra of the anion radical and dianion of 2,2'-dimethyl-1,1'-bianthryl (DMBA) were measured. The CD spectrum of the DMBA anion radical was elucidated qualitatively by a coupled oscillator model for the system including different chromophores, from which it was revealed that the unpaired electron locates in one methylanthracene moiety. The CD spectra of the neutral molecule and dianion of DMBA were also elucidated by a coupled oscillator model for the system including two equivalent chromophores. The dihedral angles ( $\alpha$ ) of the neutral molecule and dianion were estimated from the absorption bands, which were resolved by reference to the CD peaks to be about  $100^\circ$  ( $\alpha = 0$  at the cis planar configuration).

Extensive studies of the absorption spectra of ion radicals of aromatic compounds have been made both theoretically and experimentally.<sup>1</sup> The molecular orbital calculation and the method of the plane polarized light have been applied to the interpretations of the absorption bands.<sup>2-4</sup> These methods, however, have been limited to the planar ion radicals or dimer cation having a "sandwich" structure<sup>5,6</sup> and paracyclophane anion radical.<sup>7</sup> For the studies of the absorption spectra of the ion radicals having "three-dimensional" structures such as angular biaryl ion radicals, any method which could elucidate the absorption spectrum has not been developed.

On the other hand, it has been shown that the circular dichroism (CD) measurement is a useful technique for studying the stereochemistry and for the assignment of the absorption bands of the organic compounds and metal complexes.<sup>8</sup> Then, it is expected that the application of the CD measurement to the study of the ion radicals may afford useful information for the assignment of the absorption spectra and also for the estimation of the structure of the species.

Recently, Weissman and Chang reported the optical rotatory dispersion (ORD) spectra of the mono-, di-, and trianion of hexahelicene.<sup>9</sup> However, any analysis on the ORD spectra of hexahelicene anions has not been performed, since these ORD showed complicated spectra in the visible and ultraviolet regions. The simplest and most successful theory of optical activity is the coupled oscillator model, which is applicable to the biaryls.<sup>10</sup> Therefore, the biaryls may be an appropriate example for the application of the CD measurement to the study of the anion radical.

When an angular biaryl is reduced by an alkali metal, three kinds of the anion may be formed: (1) an added

electron delocalizes between both aromatic moieties, (2) an added electron localizes in one aromatic moiety, and (3) one electron is added to each of the two aromatic moieties. In our previous letter it was shown that the anion radical of 2,2'-dimethyl-1,1'-binaphthyl belongs to case 1, a delocalized anion radical.<sup>11</sup> In this paper the CD spectra belonging to cases 2 and 3 are illustrated by the anion radical and dianion of 2,2'-dimethyl-1,1'-bianthryl.

## Experimental Section

(*R*)-2,2'-Dimethyl-1,1'-bianthryl (Figure 1) was synthesized by the method of Akimoto and Yamada<sup>12</sup> ( $[\alpha]_{20D} - 276^\circ$ ). The usual high-vacuum methods for preparations of the anions were employed.<sup>4,13</sup> The CD spectra were made on a Jasco-20A dichrograph, electronic absorption spectra on a Hitachi EPS-3T spectrometer, and electron spin resonance (esr) spectra on a Hitachi 771 spectrometer. Low-temperature measurements were carried out by using a specially constructed quartz dewar. The CD and absorption spectra of the anions were shown by the absorbance rather than molar extinction coefficient ( $\epsilon$ ), since the reduction by alkali metal or  $\gamma$ -ray irradiation was not always complete.

## Results

**CD of the Neutral DMBA Molecule.** The CD and absorption spectra of (*R*)-DMBA were shown in Figure 2. The absorption spectrum of 2-methylanthracene (MA) showed a similar spectrum to that of anthracene (Figure 2). According to the notation presented by Clar,<sup>14</sup> the absorption bands of DMBA were classified into two parts: the region of  $25\text{--}33 \times 10^3 \text{ cm}^{-1}$  is the short-axis polarized transition ( $p$  band), and the region of  $35\text{--}43 \times 10^3 \text{ cm}^{-1}$  is the long-axis polarized transition ( $\beta$  band). In the  $p$ -band region, the positive CD band with the vibronic structures appeared. The extinction coefficient of the  $p$  band of DMBA is larger than that of MA. In the  $\beta$ -band region, two strong CD bands with opposed signs and nearly equal CD magnitudes were observed. The absorption band of the  $\beta$  band of DMBA was broader than that of MA. This may be corresponding to the splitting of two  $\beta$  bands of MA moieties.

**CD of the Anion Radical of DMBA.** When the 1,2-dimethoxyethane (DME) solution of (*R*)-DMBA was

(1) C. N. R. Rao, V. Klyanaraman, and H. V. George, *Appl. Spectrosc. Rev.*, **3**, 153 (1970).

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(11) O. Ito, A. Tajiri, and M. Hatano, *Chem. Phys. Lett.*, **19**, 125 (1973).

(12) H. Akimoto and S. Yamada, *Tetrahedron*, **27**, 5999 (1971).

(13) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375 (1966).

(14) E. Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1952.

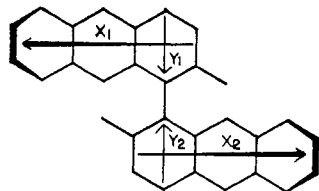


Figure 1. The coordinates system of (*R*)-bianthryl.

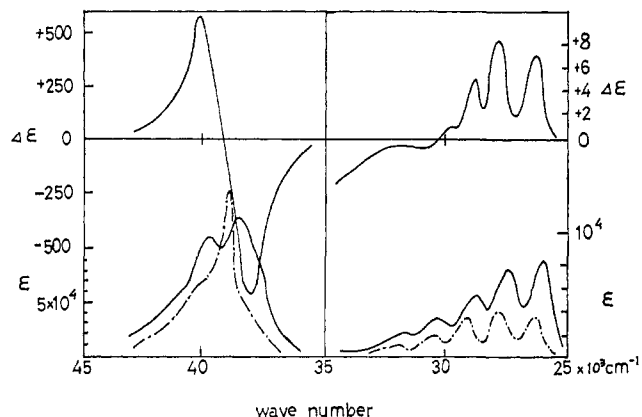


Figure 2. The CD and absorption spectra of (*R*)-DMBA (—) and absorption spectrum of MA (---);  $\Delta\epsilon = \epsilon_1 - \epsilon_r$ .

reduced by contact with a lithium metal chip in the vacuum system at the Dry Ice-methanol temperature, the solution turned blue. The CD and absorption spectra of the blue solution formed by the reduction with lithium metal were shown in Figure 3. MA also showed the blue color by the reduction with lithium metal, and the absorption spectrum of the blue solution was shown in Figure 3. When these blue solutions were warmed up to room temperature in the absence of the lithium metal chip, the color did not change. Similar spectra were observed also by the reduction with sodium metal in DME or 2-methyltetrahydrofuran (MTHF). The blue solutions of MA and DMBA exhibited the esr signals with hyperfine structures characteristic of the anion radicals of anthracene derivatives.<sup>15</sup> Then, these blue species were identified as anion radicals.

The absorption spectrum of the DMBA anion radical is divided into six parts by reference to signs in the CD extrema, since the sign of the CD band does not invert in one electronic transition. The classification of the CD bands of the DMBA anion radical was made as follows: band I ( $13.5 \times 10^3 \text{ cm}^{-1}$ ), band II ( $17.2 \times 10^3 \text{ cm}^{-1}$ ), band III ( $18\text{--}23 \times 10^3 \text{ cm}^{-1}$ ), band IV ( $25.7 \times 10^3 \text{ cm}^{-1}$ ), band V ( $27.1 \times 10^3 \text{ cm}^{-1}$ ), and band VI ( $29.8 \times 10^3 \text{ cm}^{-1}$ ). The absorption bands of the DMBA anion radical were also classified as follows: band I ( $13.7 \times 10^3 \text{ cm}^{-1}$ ), band II ( $16.6 \times 10^3 \text{ cm}^{-1}$ ), band III ( $18\text{--}23 \times 10^3 \text{ cm}^{-1}$ ), band IV ( $25.8 \times 10^3 \text{ cm}^{-1}$ ), band V ( $27.1 \times 10^3 \text{ cm}^{-1}$ ), and band VI ( $30.2 \times 10^3 \text{ cm}^{-1}$ ). Each difference between the CD peaks and corresponding absorption maxima is very small. The absorption bands of the MA anion radical were classified in a manner similar to those of the DMBA

(15) By the suggestion of a referee, we are progressing with the analysis of the esr spectra of the DMBA anion radical, which vary with solvents, alkali metals, and temperatures, on the basis of the migration of the electron spin between aromatic moieties.

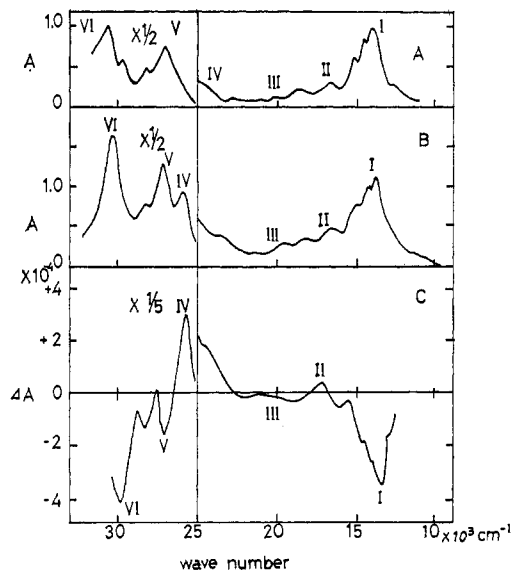


Figure 3. Optical measurements (Li-DME,  $-70^\circ$ ). (A) Absorption spectrum of the MA anion radical ( $1.5 \times 10^{-3} \text{ mol/l}$ , 2 mm cell). (B) Absorption and (C) CD spectra of the (*R*)-DMBA anion radical ( $1.6 \times 10^{-3} \text{ mol/l}$ , 2-mm cell).  $A$  = absorbance;  $\Delta A = A_1 - A_r$ .

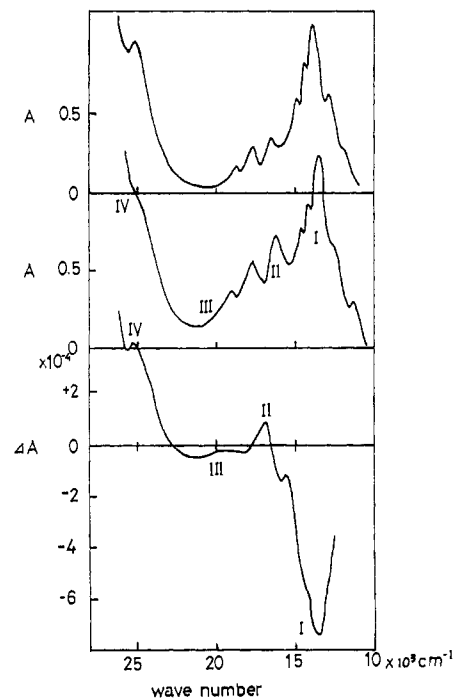


Figure 4. Absorption and CD spectra of the MA and DMBA anion radical produced by  $\gamma$ -ray irradiation in MTHF at  $-196^\circ$  ( $3 \times 10^{-3} \text{ mol/l}$ , 2-mm cell): (a) absorption spectrum of the MA anion radical; (b) absorption spectrum of the DMBA anion radical; (c) CD spectrum of the (*R*)-DMBA anion radical.

anion radical, since these absorption spectra resembled each other. When the glassy solution of (*R*)-DMBA in MTHF was irradiated by  $\gamma$ -ray at  $-196^\circ$ , the solution also turned blue. The CD and absorption spectra were shown in Figure 4, with the spectrum of the MA anion radical produced by the same method. In these spectra, the bands in the higher wave-number region than  $25 \times 10^3 \text{ cm}^{-1}$  were overlapped with those of unreacted neutral molecules. Then the spectra of the visible and infrared regions were shown in Figure 4.

Since the CD and absorption spectra of the DMBA anion radical produced by  $\gamma$ -ray irradiation were similar to those by alkali metal reduction, the same numberings of the absorption bands were made.

**CD of the Dianion of DMBA.** When the blue solution of the DMBA anion radical was reduced by further contact with alkali metal at room temperature, the solution turned green. Accompanying the color change, the CD magnitude in the higher wave-number region of band I of the DMBA anion radical decreased and the CD magnitude in the lower wave-number region of band I increased toward negative. Eventually the CD sign in the higher wave-number region of band I inverted to a positive sign ( $I_+$ ) and band I showed two splitting CD bands with opposite signs (Figure 5). In the regions of bands V and VI, a new positive CD band ( $V_+$  and  $VI_+$ ) appeared. With these changes in the CD spectrum, broadening of the absorption bands and small shifts of the absorption maxima were observed in the absorption spectrum. Moreover, accompanying the appearance of positive CD bands, the esr signal disappeared at room temperature. Then the color change from blue to green may be due to the formation of the dianion of DMBA. Although the esr spectrum of the dianion produced by sodium metal reduction in MTHF was measured at  $-196^\circ$ , any signal due to triplet state was not observed.

## Discussions

**CD of the Neutral DMBA.** The absorption bands in the  $\beta$ -band region are divided into two parts by reference to the two CD peaks (Figure 2);  $\beta_{0,-}$  with a negative CD band ( $38.0 \times 10^3 \text{ cm}^{-1}$ ) and  $\beta_{0,+}$  with a positive CD band ( $40.2 \times 10^3 \text{ cm}^{-1}$ ). The intensity of the absorption band at the lower wave number ( $\beta_{0,-}$ ) is stronger than that at the higher wave number ( $\beta_{0,+}$ ). The CD and absorption spectra of the 1,1'-bianthryls can be elucidated by a coupled oscillator model for the system including two equivalent chromophores.<sup>16,17</sup> The rotational strength ( $R_{0,\pm}$ ) and relative absorbance ( $M_{0,\pm}$ ) for the split components of the long-axis polarized transitions of the MA moieties are described as follows

$$R_{0,\pm} = \mp(\pi\bar{\nu}/2)(\mathbf{r}_{12} \cdot \mathbf{u}_1\mathbf{u}_2) \quad (1)$$

$$\tan^2(\alpha/2) = (\mathbf{u}_{0,-}/\mathbf{u}_{0,+}) \quad (2)$$

$$\mathbf{u}_{0,\pm} = 1/\sqrt{2}(\mathbf{u}_1 \pm \mathbf{u}_2) \quad (3)$$

where,  $\mathbf{u}_1$  and  $\mathbf{u}_2$  are the electric dipole moments of the long-axis polarized transitions of rings 1 and 2, respectively,  $\bar{\nu}$  is transition frequency in reciprocal centimeters,  $\mathbf{r}_{12}$  is the position vector from ring 1 to ring 2, and  $\alpha$  is the dihedral angle ( $\alpha = 0$  at the cis planar configuration). Since the interaction energy between the long-axis polarized transitions ( $\mathbf{u}_1$  and  $\mathbf{u}_2$ ), which was calculated by the dipole-dipole approximation, was positive at all dihedral angles,<sup>15</sup> the energy of the plus component was higher than that of the minus one. The sign of  $(\mathbf{r}_{12} \cdot \mathbf{u}_1\mathbf{u}_2)$  was negative at all dihedral angles for the 1,1'-bianthryls having the *R* configuration. Then, the positive CD sign predicted the higher energy component and the negative CD sign predicted the lower

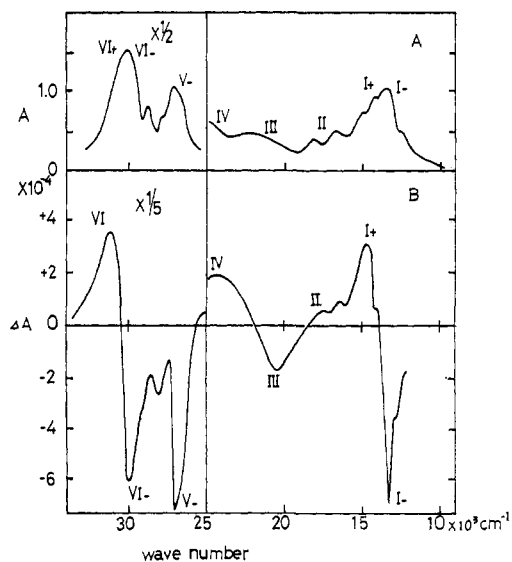


Figure 5. (A) Absorption and (B) CD spectra of the (*R*)-DMBA dianion (Li-DME,  $-70^\circ$ ,  $1.6 \times 10^{-3} \text{ mol/l}$ , 2-mm cell).

energy component. Therefore, the  $\beta_{0,+}$  band with a positive CD sign at  $40.2 \times 10^3 \text{ cm}^{-1}$  and the  $\beta_{0,-}$  band with a negative CD sign at  $38 \times 10^3 \text{ cm}^{-1}$  were attributed to the split components of the long-axis polarized transitions of the MA moieties. The following two methods may be applicable for the estimation of the dihedral angle. One of the methods is to compare the observed splitting energy ( $2200 \text{ cm}^{-1}$ ) of the  $\beta$  bands with the calculated values of the dipole-dipole interaction energy.<sup>16</sup> However, it is pointed out by many investigators<sup>18,19</sup> that the splitting energy calculated with dipole-dipole interaction approximation is about five times larger than the observed value. The simplest and most accurate method for the estimation of the dihedral angle is expected by the use of eq 2. The errors, which may emerge by resolving the overlapped bands, may be compensated for by the use of the relative intensities of the absorption bands of the split components. From this method, the dihedral angle of DMBA,  $\alpha$ , is given to be about  $100^\circ$ . This value is close to that of dimethyl-1,1'-bianthryl-2,2'-dicarboxylate ( $110^\circ$ ), whose CD and absorption spectra are similar to those of DMBA.<sup>16</sup> These results are summarized in Table I.

**CD of the Anion Radical of DMBA.** The absorption spectra of the DMBA anion radicals resemble those of the MA anion radicals (Figures 3 and 4). The similarity of these absorption spectra suggests that an added electron to DMBA localizes in one MA moiety and another MA moiety remains as a neutral molecule.<sup>20</sup> If an unpaired electron delocalizes between both MA moieties, a new absorption band due to the charge resonance should appear at lower wave number, and the absorption bands of the DMBA anion radical should shift to higher wave number than those of the MA anion radical to the amount of the charge resonance

(18) J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1964).

(19) Dipole-dipole interaction energies for the 1,1'-bianthryls were expanded in the molecular parameters by Grinter and Mason.<sup>16</sup> By this method the dihedral angle of DMBA is given to be about  $90^\circ$ .

(20) In the optical measurement a term "delocalization" was used for the anion radical of the biaryls in which the charge resonance bands caused by the splitting of the ground states of the moieties were observed. On the other hand, "localization of an added electron" was used for the system in which the charge resonance band was not observed.<sup>8-7,11</sup>

(16) R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, **60**, 274 (1964).

(17) O. E. Weigang and M. J. Nugent, *J. Amer. Chem. Soc.*, **91**, 4555 (1969).

Table I. The Assignments of the Electronic Transitions of (R)-DMBA

Band	CD		(R)-DMBA			MA	
	$\bar{\nu}_{\max}, \times 10^3 \text{ cm}^{-1}$	$\Delta\epsilon$	$\bar{\nu}_{\max}, \times 10^3 \text{ cm}^{-1}$	$\epsilon, \times 10^3$	$g,^a \times 10^{-3}$	$\bar{\nu}_{\max}, \times 10^3 \text{ cm}^{-1}$	$\epsilon, \times 10^3$
p	26.3	+6.9	25.9	7.8	+0.88	26.3	3.3
	27.8	+8.3	27.4	7.2	+1.15	27.7	3.8
	28.8	+5.0	28.7	5.2	+0.96	29.2	3.2
$\beta$	38.0	-740	38.5	113	-6.55	39.0	139
	40.2	+540	39.9	96	+5.63	40.6 <sup>b</sup>	

<sup>a</sup>  $g = \Delta\epsilon/\epsilon$ . <sup>b</sup> Shoulder.

energy, as shown in our previous study of the delocalized anion radical of 2,2'-dimethyl-1,1'-binaphthyl.<sup>7,11</sup> However, no other band, as due to charge resonance, was observed in the lower wave number and the observed shift of band I is toward the lower wave-number side compared with the corresponding band of the MA anion radical. Moreover, it is also expected for the delocalized anion radical that two CD peaks with opposite signs due to the splitting of the long-axis polarized transitions of the MA anion radical moieties should appear in the CD spectrum.<sup>11</sup> Even if bands I and II were due to these split components, the sequence of these CD signs should be opposite to the predicted one.<sup>11</sup> Then these optical measurements suggest that the added electron locates in one MA moiety. A similar result was recently reported by Hoshino, Kimura, and Imamura in the anion radical of 9,9'-bianthryl.<sup>21</sup>

The CD of the localized anion radical can be elucidated by the coupled oscillator model for the system including different chromophores.<sup>22</sup> The rotational strengths ( $R_{AP}$ ) of the transitions from the MA anion radical moiety are described as follows<sup>23</sup>

$$R_{AP} = -(2\pi/c) \frac{V_{AP, NP} \bar{\nu}_{AP} \bar{\nu}_{NP}}{h(\bar{\nu}_{AP}^2 - \bar{\nu}_{NP}^2)} (\mathbf{r}_{AN}) \cdot (\mathbf{u}_{AP} \mathbf{u}_{NP}) \quad (4)$$

$$V_{AP, NP} = \frac{\mathbf{u}_{AP} \mathbf{u}_{NP}}{\mathbf{r}_{AN}^3} - 3 \frac{(\mathbf{u}_{AP} \cdot \mathbf{r}_{AN})(\mathbf{u}_{NP} \cdot \mathbf{r}_{AN})}{\mathbf{r}_{AN}^5} \quad (5)$$

where, A and N denote the MA anion radical moiety (A) and the neutral molecule moiety (N), respectively. P is the polarization of the transition of the moiety (X for the long-axis polarized and Y for the short-axis polarized transition of the MA moiety) and  $\mathbf{r}_{AN}$  is the position vector from the anion radical moiety to the neutral molecule moiety. From the above equations the signs of CD bands are predicted qualitatively as follows. Assuming that the transitions of the MA anion radical moiety interact with the long-axis polarized transition ( $\beta$ -band) of the neutral molecule moiety,  $V_{AX, NX}$  is positive at all dihedral angles.<sup>16</sup> Then, the band arising from the long-axis polarized transitions of the MA anion radical moiety exhibits negative signs at all dihedral angles. In a similar manner, if the DMBA anion radical retains a similar dihedral angle to that of the neutral molecule (*ca.* 100°) and the short-axis polarized transitions of the MA anion radical moiety

interact with the long-axis polarized transition ( $\beta$  band) of the neutral molecule moiety, the bands arising from the short-axis polarized transitions of the MA anion radical exhibit positive CD signs. Therefore, band I of the DMBA anion radical with a negative CD sign ( $13.5 \times 10^3 \text{ cm}^{-1}$ ) could be assigned to the band arising from the long-axis polarized transition of the MA anion radical moiety ( $13.9 \times 10^3 \text{ cm}^{-1}$ ). Bands V ( $27.1 \times 10^3 \text{ cm}^{-1}$ ) and VI ( $29.8 \times 10^3 \text{ cm}^{-1}$ ) of the DMBA anion radical with negative CD signs are also assigned to the bands arising from the long-axis polarized transitions of the MA anion radical moiety,  $27.0 \times 10^3$  and  $30.5 \times 10^3 \text{ cm}^{-1}$ , respectively.<sup>24</sup> Band IV with a positive sign ( $25.7 \times 10^3 \text{ cm}^{-1}$ ) could be assigned to the band arising from the short-axis polarized transition of the MA anion radical moiety,  $24.8 \times 10^3 \text{ cm}^{-1}$ . Appearance of the positive weak CD band in the spectral region of band II ( $17.2 \times 10^3 \text{ cm}^{-1}$ ) indicates that some other bands, which are caused by the short-axis polarized transition of the MA anion radical moiety, locate in the wave-number region overlapped with a strong band I. Band III together with the weak negative CD band may be due to the impurity.<sup>25</sup>

From the above results for the DMBA anion radical, the assignments of the bands of the MA anion radical can be made as follows: band I ( $13.9 \times 10^3 \text{ cm}^{-1}$ ), band V ( $27.0 \times 10^3 \text{ cm}^{-1}$ ), and band VI ( $30.5 \times 10^3 \text{ cm}^{-1}$ ) are the long-axis polarized transitions; band II ( $16.7 \times 10^3 \text{ cm}^{-1}$ ) and band IV ( $24.8 \times 10^3 \text{ cm}^{-1}$ ) are the short-axis polarized transitions. Above assignments of the MA anion radical agree with those of the anthracene anion radical given by the plane polarized light measurement by Hoijtink and Zandstra.<sup>4</sup> These results also agree with the theoretical assignments of the anthracene anion radical by Hush and Rowlands<sup>2</sup> and Shida and Iwata.<sup>26</sup> The same assignments for the bands of the DMBA anion radical and the MA anion radical produced by  $\gamma$ -ray irradiation could also be made. It is expected that the DMBA anion radical produced by  $\gamma$ -ray irradiation in the glassy solution may retain a similar dihedral angle to that of the neutral molecule. Then, the similarity between the CD and absorption spectra of the DMBA anion radical produced by the lithium reduction and those by  $\gamma$ -ray radiolysis suggests that the dihedral angle of the DMBA anion radical produced by lithium reduction is also close to that of the neutral DMBA molecule.

(21) M. Hoshino, K. Kimura, and M. Imamura, *Chem. Phys. Lett.*, **20**, 193 (1973).

(22) I. Tinoco, Jr., *Advan. Chem. Phys.*, **4**, 113 (1962).

(23) In this equation, only the local excitations within each moiety were considered. It is expected that the contributions of the interring charge-transfer transitions to the rotational strength may be small since the electric moments of these charge-transfer transitions are nearly parallel or antiparallel to a vector  $\mathbf{r}_{AN}$  in eq 4.

(24) In the band V and VI regions, the p band of the neutral molecule moiety also may appear. However, the intensity of this band may be small compared with those of bands V and VI of the anion radical moiety.

(25) N. H. Vethorst and G. J. Hoijtink, *J. Amer. Chem. Soc.*, **87**, 4529 (1965).

(26) T. Shida and S. Iwata, *J. Amer. Chem. Soc.*, **95**, 3473 (1973).

**Table II.** The Assignments of the Electronic Transitions of the Localized Anion Radical of (*R*)-DMBA Formed by Lithium Metal Reduction in DME at  $-70^\circ$

Band	( <i>R</i> )-DMBA anion radical		Transition	MA anion radical $\bar{\nu}_{\max}$ , $\times 10^3 \text{ cm}^{-1}$
	$\bar{\nu}_{\max}$ , $\times 10^3 \text{ cm}^{-1}$	$g$ , $\times 10^{-4}$		
I	13.5	-3.2	$^2a^-$	13.9
II	17.2	+1.7	$^2p^-$	16.7
III	18-23			
IV	25.7	+8.8	$^2b^-$	24.8
V	27.1	-2.5	$^2\alpha_1^-$	27.0
VI	39.8	-6.7	$^2\alpha_2^-$	30.5

**CD of the DMBA Dianion.** Two kinds of dianion may be expected for the DMBA dianion. One of them is the localized dianion, in which the second electron is added to the MA anion moiety in the DMBA anion radical. If the localized dianion is formed, the absorption band of the DMBA anion radical may disappear and new absorption bands which arise from the MA dianion may appear at a higher wave number.<sup>4</sup> However, the observed absorption spectrum of the DMBA dianion did not change essentially compared with that of the DMBA anion radical. Then the dianion of DMBA may be formed by the addition of the second electron to the MA neutral molecule moiety in the DMBA anion radical. The CD and absorption spectra in such a dianion could be elucidated by a coupled oscillator model for the system including two equivalent chromophores, which is described by eq 1 and 2. The predicted sequence of the CD signs for the split components of the long-axis polarized transition of the MA anion radical moiety is negative to positive from the lower to higher wave number. For the transition of the DMBA dianion arising from the combination of the short-axis polarized transitions of the MA anion radical moiety, the sign of the CD band could not be predicted from this theory. However, it is expected that this sign may be the same as that of the short-axis polarized transition of the neutral molecule (p band), positive CD sign (Figure 2). Then, a positive sign may be expected for the short-axis polarized transition of the DMBA dianion.

The absorption bands of the DMBA dianion (Figure 5) could be divided as follows: band I ( $13.6 \times 10^3 \text{ cm}^{-1}$ ), band II ( $18.2 \times 10^3 \text{ cm}^{-1}$ ), band III ( $20-22 \times 10^3 \text{ cm}^{-1}$ ), band IV ( $25.0 \times 10^3 \text{ cm}^{-1}$ ), band V ( $27.1 \times 10^3 \text{ cm}^{-1}$ ), and band VI ( $30.2 \times 10^3 \text{ cm}^{-1}$ ). The CD extrema, however, could be divided into eight parts as follows: band I<sub>-</sub> ( $13.3 \times 10^3 \text{ cm}^{-1}$ ), band I<sub>+</sub> ( $14.9 \times 10^3 \text{ cm}^{-1}$ ), band II ( $17.4 \times 10^3 \text{ cm}^{-1}$ ), band III ( $20.4 \times 10^3 \text{ cm}^{-1}$ ), band IV ( $24.4 \times 10^3 \text{ cm}^{-1}$ ), band V<sub>-</sub> ( $26.8 \times 10^3 \text{ cm}^{-1}$ ), band VI<sub>-</sub> ( $29.8 \times 10^3 \text{ cm}^{-1}$ ), and band VI<sub>+</sub> ( $31.3 \times 10^3 \text{ cm}^{-1}$ ). The assignments of these CD bands are made by comparing with the predicted signs of the CD bands. Negative CD band I<sub>-</sub> and positive CD band I<sub>+</sub> agree with the predicted sequence of the CD signs for the split components of the long-axis polarized transition of the MA anion radical moiety. Then the absorption band I of the DMBA dianion could be resolved into two components, band I<sub>-</sub> and band I<sub>+</sub>. From the same reasoning, negative CD band VI<sub>-</sub> and positive CD band VI<sub>+</sub> are assigned to split components of the long-axis polarized transition of the MA anion radical moiety. Then the absorption band VI could be

resolved into two components, band VI<sub>-</sub> and band VI<sub>+</sub>. Although band V of the DMBA dianion may contain two split components, one of the CD bands is probably overlapped with the CD band VI<sub>-</sub>. Then only band V<sub>-</sub> with negative CD sign is observed in the CD spectrum. Bands II and IV with a single positive CD sign are assigned to the bands arising from the minus combination of the short-axis polarized transitions of the MA anion radical moieties, since the short-axis polarized transition of the neutral molecule (p band) also shows a positive CD band. The CD band in the region of band III decreased when the solution was warmed up to room temperature, while the CD magnitudes of the other bands did not change. The absorbance of band III did not change with raising the temperature. Then this band may be due to other species such as hydride species which may easily racemize at room temperature. Above assignments of the absorption bands of the DMBA dianion lead to the assignments of the absorption bands of the MA anion radical as follows: bands I, V, and VI are the long-axis polarized transitions, and bands II and IV are the short-axis polarized transitions (Figure 2). These results agree with the assignments of the absorption bands of the MA anion radical which were made by the aid of the CD spectrum of the DMBA anion radical in a preceding section. Therefore, the assignments of the bands of the MA anion radical from the CD spectrum of the DMBA dianion agree with those by the measurements of the plane polarized light for the anthracene anion radical by Hoiijtink and Zandstra<sup>4</sup> and with the theoretical result for the anthracene anion radical by Hush and Rowlands<sup>2</sup> and Shida and Iwata.<sup>26</sup> These results are summarized in Table III.

**Table III.** The Assignments of the Electronic Transitions of (*R*)-DMBA Dianion Formed by Lithium Metal Reduction in DME at  $-70^\circ$

Band	( <i>R</i> )-DMBA dianion		Transition	MA anion radical $\bar{\nu}_{\max}$ , $\times 10^3 \text{ cm}^{-1}$
	$\bar{\nu}_{\max}$ , $\times 10^3 \text{ cm}^{-1}$	$g$ , $\times 10^{-4}$		
I <sub>-</sub>	13.3	-6.4	$^2a^-$	13.9
I <sub>+</sub>	14.9	+7.1		
II	17.4	+2.0	$^2p^-$	16.7
III	20.4		(Hydride)	
IV	24.4	+2.9	$^2b^-$	24.8
V <sub>-</sub>	26.8	-17.5	$^2\alpha_1^-$	27.0
V <sub>+</sub>				
VI <sub>-</sub>	29.8	-11.5	$^2\alpha_2^-$	30.5
VI <sub>+</sub>	31.3	+8.8		

To ascertain the identification of the DMBA dianion from the signs in the CD spectrum, it is necessary to compare the observed CD magnitudes with theoretical rotational strengths. The ratio of the rotational strength of the neutral molecule ( $R(\text{neutral})$ ) to that of dianion ( $R(\text{dianion})$ ) can be obtained from eq 1, assuming that the dihedral angles of both species were the same

$$R(\text{neutral})/R(\text{dianion}) = \bar{\nu}_N |\mu_N|^2 / \bar{\nu}_A |\mu_A|^2 \quad (6)$$

where, N and A denote the MA neutral molecule and MA anion radical moieties, respectively. By using the absorption maximum of the  $\beta$  band of MA shown in Figure 1 ( $\epsilon$  13,900 at  $39,000 \text{ cm}^{-1}$ ) and that of band I

of the anthracene anion radical reported by Paul, Lipkin, and Weissman<sup>27</sup> ( $\epsilon$  9000 at 14,000  $\text{cm}^{-1}$ ),  $R$ -(neutral)/ $R$ -(dianion) was calculated to be 44. This value was comparable to the observed ratio of the anisotropy factors of both species,  $g$ -(neutral)/ $g$ -(dianion) = *ca.* 55.<sup>28</sup> These values support the identification of the dianion and the above assignments of the electronic transition.

The dihedral angle of the DMBA dianion may be given by eq 2. By substituting the intensities of the absorption bands  $I_-$  and  $I_+$ , which were resolved by reference to each CD maxima, into eq 2, the dihedral angle of the dianion was estimated to be *ca.* 100°. The same value is obtained from the split components of band VI and bands  $VI_-$  and  $VI_+$ . This value is the same as that of the neutral molecule which is estimated by the same method. In general, it may be expected that the dihedral angle of the dianion may be opened toward trans planar by the electrostatic repulsion force between the MA anion radical moiety. The estimated

(27) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956).

(28) The smaller value of the observed ratio indicates that the observed CD magnitude of the DMBA dianion was smaller than that of the DMBA neutral molecule, since the smaller the splitting energy with the dipole-dipole interaction the larger the compensation of the CD magnitudes with the opposite signs.

dihedral angles, however, are not different between the dianion and the neutral molecule. This implies that the MA (or the MA anion radical) moieties in DMBA (or the DMBA dianion) cannot rotate about the 1,1' band due to large steric hindrance. Indeed any racemization process was not observed both for the neutral molecule and the dianion.

Above discussions can be applied to the dianions which exist in both the triplet state and the singlet state. It is pointed out in the literature that the dianion exists in the triplet state only when the dianion has higher symmetry than  $D_{2d}$ .<sup>21,29</sup> The dianions of bis(2,2'-biphenyl)methane<sup>29</sup> and 9,9'-bianthryl<sup>21</sup> exist in the triplet state, since they contain two planar conjugated systems which are perpendicular to each other. In the case of the DMBA dianion, any esr signal was not observed in the green glassy solution. This indicates that the DMBA dianion exists in the singlet state, which corresponds with the fact that the dihedral angle of the DMBA dianion is not 90° but *ca.* 100°.

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(29) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Chem. Phys.*, **39**, 2028 (1963).

## Low-Lying Electronic States of Biacetyl

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**Abstract:** Absorption and emission spectra of biacetyl- $h_6$  in the visible region have been reexamined at 4–8 K° in the polycrystalline state. The observations in absorption confirm all the important features reported in the 1955 study by Sidman and McClure, and the vibrational analysis of the  ${}^1A_u \leftarrow {}^1A_g$  and  ${}^3A_u \leftarrow {}^1A_g$  band systems, though different in a few details, is similar to that given by these authors. However, the two long-lived emission systems described in the earlier work are due to chemical impurities, and the true  ${}^3A_u \leftarrow {}^1A_g$  phosphorescence is described and analyzed vibrationally. Evidence for an absorption system corresponding to a singlet-singlet electronic transition of a cis or skew rotational isomer is discussed. The biacetyl crystal is photosensitive and the intensity of long-lived impurity emission is enhanced by exposure to wavelengths below 490 nm. The fluorescence and phosphorescence lifetimes measured for crystalline biacetyl- $h_6$  at 6°K are, respectively,  $12 \pm 1$  nsec and  $2.5 \pm 0.2$  msec.

Although biacetyl (2,3-butanedione) has many photo-physical and photochemical applications, its lower excited states have never been fully characterized. The visible absorption of biacetyl (BA) vapor is discrete but extremely complex owing to the thermal distribution of molecules over many levels of the low-lying torsional modes and has not been analyzed.<sup>2a</sup> Our knowledge of the lower electronic states therefore depends on the analysis of the crystal spectrum carried out in 1955 by Sidman and McClure (SM)<sup>3</sup> who established that the principal absorption bands belong to the  $\pi^* \leftarrow n_-$

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(2) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966: (a) p 561, (b) p 538.

(3) J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, **77**, 6461, 6471 (1955).

electronic transitions  ${}^1A_u \leftarrow {}^1A_g$  and  ${}^3A_u \leftarrow {}^1A_g$  of *trans*-BA, the 0–0 bands occurring near 437 and 490 nm, respectively, in the solid at low temperatures. Evidence was also obtained for a third absorption system tentatively identified by SM with the singlet-singlet  $\pi^* \leftarrow n_+$  electronic transition  ${}^1B_g \leftarrow {}^1A_g$ , and an absorption peak at 447 nm ( $22,359 \text{ cm}^{-1}$ ) was assigned to a vibronic origin of this system. Although the crystal structure of BA is not known, observations of the factor-group splittings in the vibrational spectrum suggest that *trans*-BA molecules occupy  $C_i$  sites in the solid, probably in a  $C_{2h}$  space group.<sup>4</sup> In this case the g, u classification of states is rigorous in the crystal and the pure  ${}^1B_g \leftarrow {}^1A_g$  electronic transition is allowed (*xyz* polar-

(4) J. R. Durig, S. E. Hannum, and S. C. Brown, *J. Phys. Chem.*, **75**, 1946 (1971).