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Polarized Absorption Spectra of Aromatic Radicals in Stretched Polymer Film. IV. Radical Ions of 9-Substituted Anthracenes

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Radical ions of some 9-substituted anthracene derivatives have been prepared in polymer film by γ-irradiation at 77 K. By use of the polarized absorption spectra of these radical ions, the absorption spectra have been resolved into two components (resolved spectra), the transition moments of which are polarized parallel to the molecular long and short axes, respectively. Correlation of the characteristic absorption bands is discussed briefly.

In previous papers we have shown that the stretched film technique combined with γ-irradiation is available for the polarization measurement of the radical ions of anthracene and pyrene,[1] and acridine and phenazine.[2] By qualitative analysis of the polarized absorption spectra, the polarization direction of the electronic transition band was determined and the assignments of the bands were carried out for these radical ions.

We note here the efficient preparation method for the radical ions in the films. Radical anions are produced by γ-irradiation of the poly(vinyl alcohol) film containing the solvent *s*-butylamine and the solute aromatic molecule (PVA–BuA system). For the preparation of the cation, a poly(vinyl chloride) film containing *s*-butyl chloride and aromatic molecule is irradiated (PVC–BuCl system). In order to remove the absorption due to solvated electron or positive hole, it is essential to dope the film with enough solute ($\approx 10^{-2}$ mol dm^{-3}).

In this paper we apply this method to 9-substituted anthracenes and examine the applicability of the method. Furthermore, stretched films were used and the polarized absorption spectra of the radical ions were determined and analyzed quantitatively. The resultant resolved spectra are used to discuss the correlation of the electronic transition bands in the visible region.

Experimental

Commercially available reagents, 9-methylanthracene (G.R. grade of Tokyo Kasei Co. Ltd.) and 9-bromo-, 9-nitro-, and 9-cyanoanthracene (Aldrich Chemical Co., Inc.), were used. 9-Aminoanthracene was synthesized according to the literature.[3] Poly(vinyl alcohol) film (PVA), 0.2 mm thick, and poly(vinyl chloride) film (PVC), 0.18 mm thick, were employed as before.[1] Parent compounds were doped into PVA film with the aid of a solvent, *s*-butylamine (G.R. grade of Tokyo Kasei Co. Ltd.), and into PVC film by use of *s*-butyl chloride (G.R. grade of Tokyo Kasei Co. Ltd.). For the measurement of the polarized absorption spectra, sample films PVA and PVC were stretched 3 and 4 times, respectively. These films were irradiated by ^{60}Co γ-rays for 2 h at 77 K with a dose rate of 1.0×10^6 rad/h. Absorption spectra were measured in the range from 300 to 850 nm with a JASCO SS-50 spectrophotometer equipped with a Rochon polarizer. MO calculations were carried out for the radical ions after Zahradník and Čársky.[4] Parameters used were taken from Ishitani and Nagakura.[5]

Results and Discussion

Identification of the Absorption Spectra. *9-Methylanthracene*: Figures 1a and 1b show the absorption spectra of the γ-irradiated PVA–BuA and PVC–BuCl systems of 9-methylanthracene, respectively. Dodd has reported that the characteristic absorption maxima of the 9-methylanthracene radical anion and the cation are respectively at 13750 cm^{-1} in tetrahydrofuran and at 14050 cm^{-1} in boric acid glass.[6] These maxima are well correspondent to the absorption peak at 13.7×10^3 cm^{-1} in Fig. 1a and that at 14.2×10^3 cm^{-1} in Fig. 1b. In addition to this, these spectra resemble strongly those of the anthracene radical anion ($A^{-\cdot}$) and the cation ($A^{+\cdot}$) in the same systems.[1] Therefore the spectra of Figs. 1a and 1b are attributed to the 9-methylanthracene radical anion ($MA^{-\cdot}$) and the cation ($MA^{+\cdot}$), respectively.

9-Bromoanthracene: Figures 1c and 1d show the absorption spectra of the γ-irradiated PVA–BuA and the PVC–BuCl systems of 9-bromoanthracene, respectively. These spectra are similar to those of the 9-bromoanthracene radical anion ($BA^{-\cdot}$) in an organic glass[7]

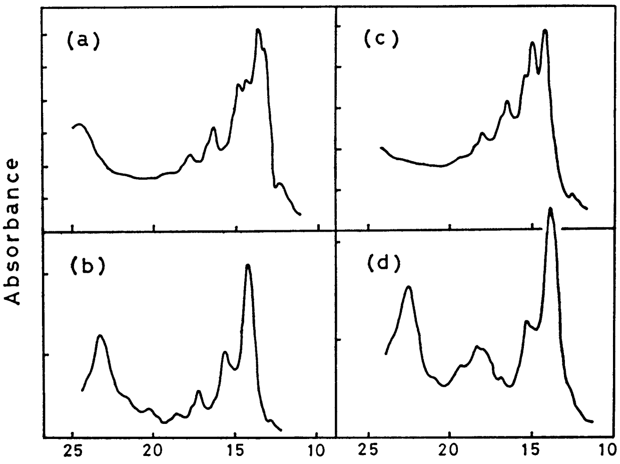

Fig. 1. Absorption spectra of 9-methylanthracene in the γ-irradiated PVA (a) and PVC (b) films, and 9-bromoanthracene in the irradiated PVA (c) and PVC (d) films, respectively.

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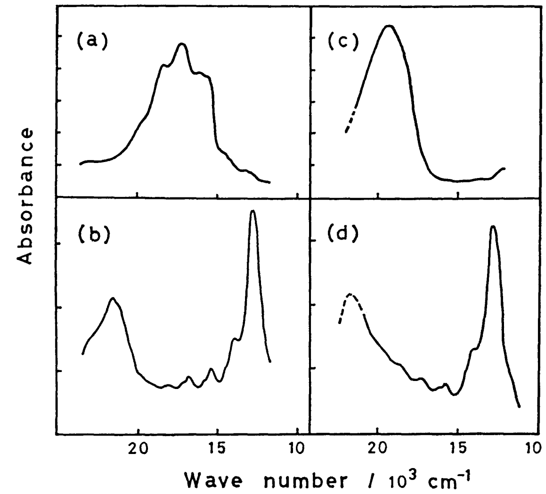

Fig. 2. Absorption spectra of 9-cyanoanthracene in the γ-irradiated PVA (a) and PVC (b) films, and 9-nitroanthracene in the irradiated PVA (c) and PVC (d) films, respectively.

and of the cation ($BA^{+\cdot}$) in a glass of 1:4 butyl chloride–methylcyclohexane.[8] Therefore, the absorption spectra of the PVA–BuA and PVC–BuCl systems are ascribed to $BA^{-\cdot}$ and $BA^{+\cdot}$, respectively.

9-Cyano-, 9-Nitro-, and 9-Aminoanthracene: Figures 2a and 2c show the absorption spectra of 9-cyano- and 9-nitroanthracene in the γ-irradiated PVA–BuA system, respectively. The spectrum of Fig. 2a resembles that of the 9-cyanoanthracene radical anion ($CA^{-\cdot}$) in dimethoxyethane, reported by Panayotov and Tsvetanov,[9] and is attributed to $CA^{-\cdot}$. The spectrum of Fig. 2c is quite different from those of $A^{-\cdot}$, $MA^{-\cdot}$, $BA^{-\cdot}$, and $CA^{-\cdot}$. As is shown in the following section, however, the resolved spectra (Fig. 5) are reasonably explained by the result calculated for the 9-nitroanthracene radical anion ($NA^{-\cdot}$). Therefore this spectrum is attributed to $NA^{-\cdot}$.

Figures 2b, 2d, and 6a show the resultant absorption spectra of 9-cyano-, 9-nitro-, and 9-aminoanthracene in the γ-irradiated PVC–BuCl systems, respectively. The former two spectra are similar to each other and also to those of $A^{+\cdot}$ and $MA^{+\cdot}$. These spectra are explained by MO calculations on the corresponding radical cations and are ascribed to their radical cations, $CA^{+\cdot}$ and $NA^{+\cdot}$. The spectrum of Fig. 6a is different from those of the other 9-substituted anthracene cations. The MO calculation for the 9-aminoanthracene radical cation ($AA^{+\cdot}$), however, explains this spectrum. Hence, this is attributed to $AA^{+\cdot}$.

Resolved Spectra. According to the symmetry of the 9-substituted anthracenes, the $\pi^*\leftarrow\pi$ electronic transition should be polarized parallel to the long or short axis in the molecular plane. By use of the polarized absorption spectra, the absorption spectrum can be resolved into two components (resolved spectra), the transition moments of which are polarized along the long and short axes.

The absorption spectrum of the symmetric and stable molecule in the PVA film can be resolved by the so-called one-parameter method developed by one of us (Y. Tanizaki).[10] This method requires the values of the stretch ratio (*Rs*) of the film and the dichroic ratio ($Rd{:}=A_{/\!/}/A_{\perp}$). In our experiment, however, we could not determine the *Rs* value in the same manner as for the stable molecule because a considerable amount of the solvent, *s*-butylamine or *s*-butyl chloride, is reserved in the film for efficient preparation of the radical ions. Therefore the one-parameter method is not applicable to our case. Instead, the two-parameter method proposed by Margulies and Yogev is applied.[11] This method requires two extreme Rd values of the pure long and short axis polarized transition bands. This may be considered to be a special case of the method given by Thulstrup *et al.*[12]

The resolved spectra, A_l and A_s, are obtained by resolving the absorption spectrum A according to the following equations:

$$A_l = \frac{Rd-Rd^s}{Rd^l-Rd^s}\cdot\frac{Rd^l+2}{Rd+2}\cdot A$$

$$A_s = \frac{Rd^l-Rd}{Rd^l-Rd^s}\cdot\frac{Rd^s+2}{Rd+2}\cdot A,$$

where Rd^l and Rd^s are two extreme *Rd* values of the pure long and short axis polarized bands, respectively. These equations are equivalent to Eqs. 42 and 43 of Ref. 11.

In the case of the anthracenes discussed here, the long and short axes are respectively the Y and Z axes, and A_l and A_s are written as A_Y and A_Z. In the following discussion the resultant resolved spectra (A_Y and A_Z) are shown without showing the polarized absorption spectra.

As shown in Figs. 1 and 2, the absorption spectra of 9-substituted anthracenes resemble each other, except for $CA^{-\cdot}$, $NA^{-\cdot}$, and $AA^{+\cdot}$. There are characteristic bands in the region $(13\text{—}14)\times10^3\,\mathrm{cm}^{-1}$ and $(22\text{—}24)\times10^3\,\mathrm{cm}^{-1}$. Considering the *Rd* curve behavior and the results of MO calculations, these bands are respectively assigned to Y and Z axis polarized transitions.[1] These absorption bands, however, are overlapped with other weak transition bands and are not considered to be "pure electronic transition bands." In order to calculate the resolved spectra, several sets of parameters (Rd^l and Rd^s) have been chosen by reference to the *Rd* values of these bands. A similar procedure has been taken for the cases of $CA^{-\cdot}$, $NA^{-\cdot}$ and $AA^{+\cdot}$. For these parameter sets, no marked changes were seen in the characteristics of the resolved spectra. Therefore one of the representative results is presented for each radical ion. These are shown in Figs. 3—6.

Anthracene: Figures 3a and 3b show the resolved spectra of $A^{-\cdot}$ and $A^{+\cdot}$. These are obtained by use of the polarized absorption spectra reported previously (Figs. 3 and 4 in Ref. 1). These resemble each other and are well explained by the calculated results shown at the bottom. For example, the intense A_Y band at $13.7\times10^3\,\mathrm{cm}^{-1}$ and A_Z band at $24.7\times10^3\,\mathrm{cm}^{-1}$ of $A^{-\cdot}$ are assigned to ${}^2B_{1g}\leftarrow{}^2B_{3u}$ and ${}^2B_{2g}\leftarrow{}^2B_{3u}$ transitions, respectively. The very weak absorption below $13.0\times10^3\,\mathrm{cm}^{-1}$ is ascribed to the forbidden transition (${}^2A_u\leftarrow{}^2B_{3u}$). In addition to these bands, a relatively weak

A_Z band is clearly distinguished in the region (15—20) × 10^3 cm^{-1}. This is assigned to the first $^2B_{2g}\leftarrow{}^2B_{3u}$ transition, as has been predicted in the previous paper.1) Similar assignments are carried out for $A^{+\cdot}$ and these results are summarized in Table 1.

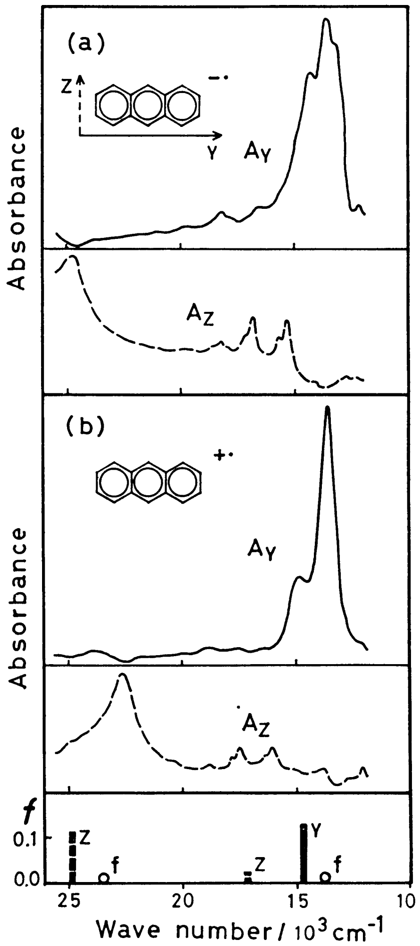

Fig. 3. Resolved spectra of anthracene radical anion (a) and cation (b).
Rd^1 and *Rd*^{s} values used are 2.85 and 0.89 for (a), and 1.75 and 0.89 for (b), respectively. A_Y and A_Z represent the components polarized parallel to the long and short axes, respectively. Calculated results are shown in the bottom, where f means forbidden transition.

9-Methyl- and 9-Bromoanthracene: Figures 4a and 4b show the resolved spectra of $MA^{-\cdot}$ and $MA^{+\cdot}$. These spectra are very similar to those of $A^{-\cdot}$ and $A^{+\cdot}$. In the A_Z spectrum of $MA^{+\cdot}$, a weak band is found in the region (20—22) × 10^3 cm^{-1} in addition to the characteristic bands. This is related to the second forbidden transition of $A^{+\cdot}$.

Figures 4c and 4d show the resolved spectra of $BA^{-\cdot}$ and $BA^{+\cdot}$. These spectra are also similar to those of $A^{-\cdot}$ and $A^{+\cdot}$, respectively. In A_Z spectrum of $BA^{+\cdot}$, an extra absorption appears in the region (17—21) × 10^3 cm^{-1}. But we are not yet able to assign this band.

9-Cyano- and 9-Nitroanthracene: Figures 5a and 5b show the resolved spectra of $CA^{-\cdot}$ and $CA^{+\cdot}$. The calculated results for these ions are also shown at the bottom. Spectra of $CA^{+\cdot}$ resemble those of $A^{+\cdot}$, while those of $CA^{-\cdot}$ are rather different from those of $A^{-\cdot}$. The latter spectra are explained by the calculated result as follows. The first weak A_Y band below 15 × 10^3 cm^{-1} is assigned to the first Y-polarized transition.

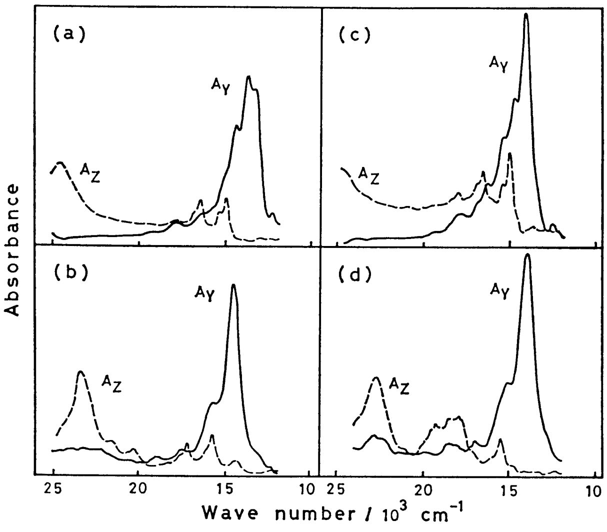

Fig. 4. Resolved spectra of 9-methylanthracene radical anion (a) (*Rd*^{1} = 1.95, *Rd*^{s} = 0.95) and cation (b) (1.65, 0.99), and 9-bromoanthracene anion (c) (2.10, 0.98) and cation (d) (1.41, 0.99).

TABLE 1. CALCULATED AND EXPERIMENTAL RESULTS FOR ANTHRACENE RADICAL IONS$^{a)}$

	Transition energy (× 10^3 cm^{-1})			Polarization$^{b)}$			Symmetry		Oscillator strength (Calcd)
	Calcd	Obsd		Calcd	Obsd				
		Anion$^{c)}$	Cation$^{d)}$		Anion	Cation	Anion	Cation	
1	13.7	<13.0	<13.0	f			Au	B_{1g}	0.000
2	14.7	13.7	13.6	Y	Y	Y	B_{1g}	A_u	0.131
3	17.1	15.4	16.0	Z	Z	Z	B_{2g}	B_{3u}	0.023
4	23.5			f			B_{3u}	B_{2g}	0.000
5	24.8	24.7	22.6	Z	Z	Z	B_{2g}	B_{3u}	0.114
6	26.7			f			A_u	B_{1g}	0.000

a) Calculated result is available for the radical anion and cation. b) Y and Z are molecular long and short axes, respectively; f means that the transition is forbidden. c) In γ-irradiated poly(vinyl alcohol) film. d) In γ-irradiated poly(vinyl chloride) film.

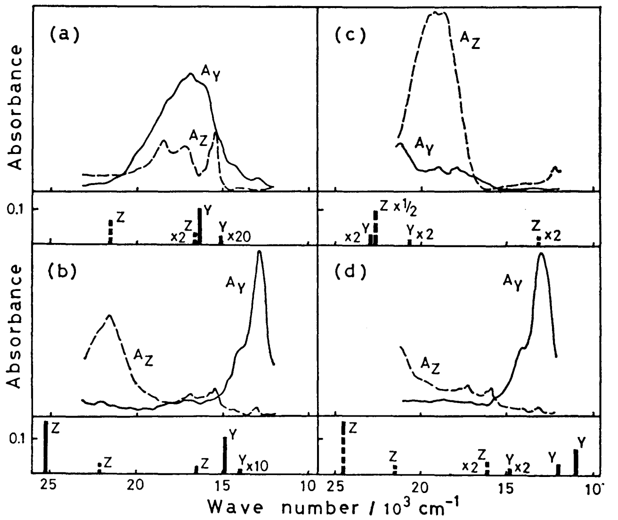

Fig. 5. Resolved spectra of 9-cyanoanthracene radical anion (a) ($Rd^1=1.68$, $Rd^s=0.99$) and cation (b) (1.51, 0.99), and 9-nitroanthracene anion (c) (1.20, 0.88) and cation (d) (1.44, 0.99). Calculated results are shown in the bottom.

The sharp A_Z peak at 15.5×10^3 cm^{-1} should be assigned to the first Z-polarized transition. The broad intense A_Y band in the region $(15—20)\times10^3$ cm^{-1} is ascribed to the second Y-polarized transition. The A_Z peak at about 18.5×10^3 cm^{-1} is tentatively assigned to the second Z-polarized transition.

Figures 5c and 5d show the resolved spectra of $NA^{-\cdot}$ and $NA^{+\cdot}$. Spectral characteristics of $NA^{+\cdot}$ are similar to those of $A^{+\cdot}$, while those of $NA^{-\cdot}$ are quite different from those of other anions. The $NA^{-\cdot}$ spectra are, however, analyzed based on the result calculated for $NA^{-\cdot}$ as follows. The A_Z band below 15×10^3 cm^{-1} and the intense A_Z band in the region $(17—21)\times10^3$ cm^{-1} are assigned to the first and the second Z-polarized transitions. The A_Y band in the region $(16—20)\times10^3$ cm^{-1} and that above 20×10^3 cm^{-1} are assigned to the first and the second Y-polarized transitions. Thus the spectrum of Fig. 2c is reasonably attributed to $NA^{-\cdot}$.

9-Aminoanthracene: Figure 6b shows the resolved spectra of $AA^{+\cdot}$. These spectra are quite different from those of other cations. These are explained by the calculated result as follows. The A_Y band below 17×10^3 cm^{-1} and the intense A_Y band in the region $(17—21)\times10^3$ cm^{-1} are ascribed to the first and the second Y-polarized transitions. A_Z bands in the region $(15.5—18)\times10^3$ cm^{-1} and at about 20×10^3 cm^{-1} are attributed to the first and the second Z-polarized transitions.

Correlation of Electronic Transition Bands. As is discussed in the section about the resolved spectra, the three characteristic absorption bands of anthracene radical ions are correlated respectively to those of the substituted anthracene ions. This situation is shown in Fig. 7, where full and open columns represent the A_Y and A_Z bands, respectively. Their positions show the absorption maximum or first peak of the bands. The spectra of $CA^{-\cdot}$, $NA^{-\cdot}$, and $AA^{+\cdot}$ have a different appearance than those of other ions. Therefore the electronic transitions of these ions are discussed qualitatively by making reference to SCF MO's of $A^{-\cdot}$ and $A^{+\cdot}$.

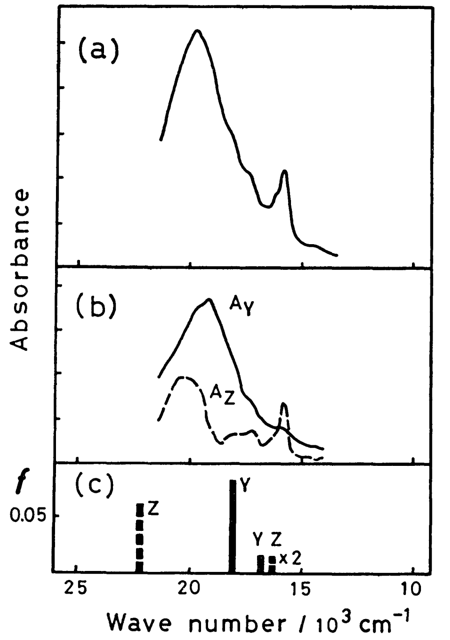

Fig. 6. Absorption spectrum of 9-aminoanthracene in the γ-irradiated PVC film (a) and its resolved spectra (b) ($Rd^1=1.42$, $Rd^s=0.90$).
Calculated results are shown in the bottom.

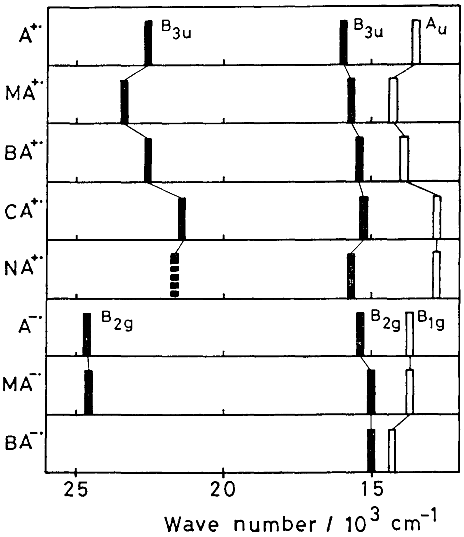

Fig. 7. Correlation diagram of the characteristic absorption bands of 9-substituted anthracenes in the visible region.
Full and open columns represent the short axis- and long axis-polarized transition bands, respectively.

SCF MO's related to the visible absorptions of $CA^{-\cdot}$ and $NA^{-\cdot}$ are shown in Fig. 8, and are correlated with those of $A^{-\cdot}$. The correlation of MO's of $CA^{-\cdot}$ (or $NA^{-\cdot}$) with those of $A^{-\cdot}$ is obtained by expanding the wavefunctions of $CA^{-\cdot}$ (or $NA^{-\cdot}$) by those of $A^{-\cdot}$ and substituent group, as follows:

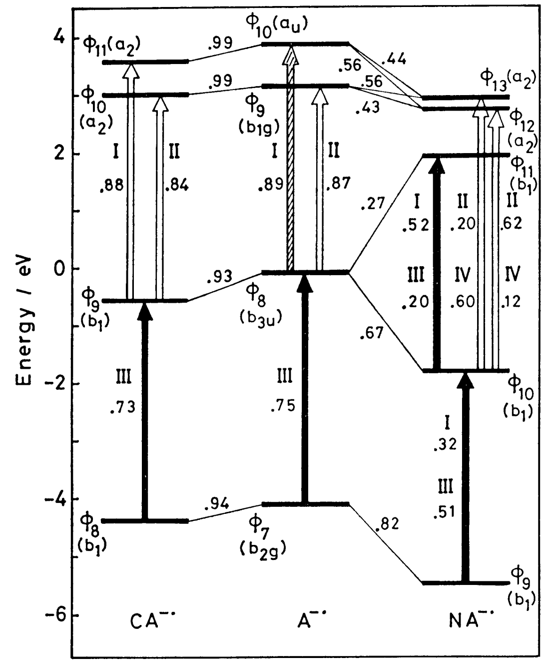

Fig. 8. Correlation diagram of MO's of 9-cyano and 9-nitroanthracene radical anions ($CA^{-\cdot}$ and $NA^{-\cdot}$) with those of anthracene radical anion ($A^{-\cdot}$). The figures along the joining fine lines are contribution weight from the MO's of $A^{-\cdot}$ to those of $CA^{-\cdot}$ and $NA^{-\cdot}$. The figures along the vertical arrows are contribution weight from the configuration to each transition. See text.

$$\phi_l(CA^{-\cdot} \text{ or } NA^{-\cdot}) = \sum_m C^l_m\phi_m(A^{-\cdot}) + \sum_n C^l_n\phi_n(\text{CN or } NO_2).$$

Contribution of ϕ_m ($A^{-\cdot}$) to $\phi_l(CA^{-\cdot}$ or $NA^{-\cdot})$ is given by the square of the coefficient, $(C^l_m)^2$. These values are shown along the correlating lines between MO's.

It is found that ϕ_8, ϕ_9, ϕ_{10}, and ϕ_{11} of $CA^{-\cdot}$ are well correlated to ϕ_7, ϕ_8, ϕ_9, and ϕ_{10} of $A^{-\cdot}$, respectively. The contribution of CN group-MO is less than 7% for these MO's. These MO's are related to the main configurations of the visible transitions of $CA^{-\cdot}$ and $A^{-\cdot}$ as follows:

$$\Psi_{I}(A^{-\cdot}) = (0.89)^{1/2}\Phi_{8-10} + \cdots \qquad (^2A_u \leftarrow {}^2B_{3u})$$
$$\Psi_{II}(A^{-\cdot}) = (0.87)^{1/2}\Phi_{8-9} + \cdots \qquad (^2B_{1g} \leftarrow {}^2B_{3u})$$
$$\Psi_{III}(A^{-\cdot}) = (0.75)^{1/2}\Phi_{7-8} + \cdots \qquad (^2B_{2g} \leftarrow {}^2B_{3u})$$
$$\Psi_{I}(CA^{-\cdot}) = (0.88)^{1/2}\Phi_{9-11} + \cdots$$
$$\Psi_{II}(CA^{-\cdot}) = (0.84)^{1/2}\Phi_{9-10} + \cdots$$
$$\Psi_{III}(CA^{-\cdot}) = (0.73)^{1/2}\Phi_{8-9} + \cdots .$$

Contributions of these configurations (squares of the coefficient) are also shown along the vertical transition arrows. Considering these contributions and correlation of MO's, it is understood that the first three transitions of $CA^{-\cdot}$ are well correlated with those of $A^{-\cdot}$. But it should be noticed here that the energy depression of $\phi_8(A^{-\cdot})$ is larger than those of the other MO's($A^{-\cdot}$) on CN group substitution. Therefore the transition energies of I and II transitions increase, while that of III decreases. As a result these transition bands overlap one another and the appearance of the $CA^{-\cdot}$ spectrum is different from those of other anions.

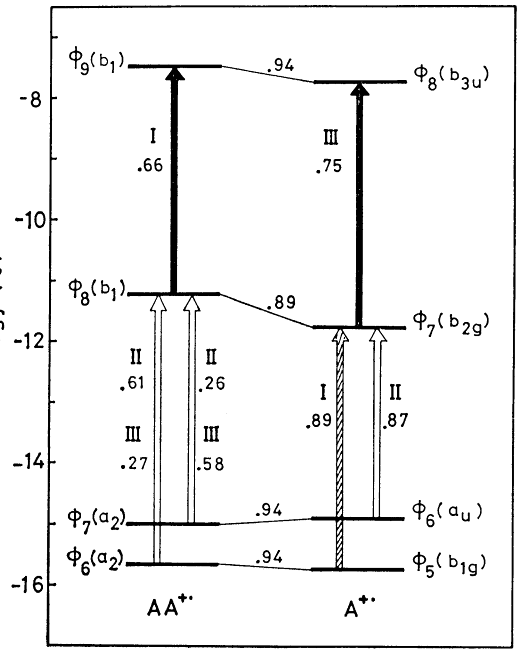

Fig. 9. Correlation diagram of MO's of 9-aminoanthracene ($AA^{+\cdot}$) and anthracene radical cations ($A^{+\cdot}$). See the captions of Fig. 8.

In the case of $NA^{-\cdot}$, the situation is quite different. The most characteristic point is the great participation of the vacant orbital of NO_2 in the visible transitions. Contributions from NO_2 vacant orbital to $\phi_9(NA^{-\cdot})$ and $\phi_{10}(NA^{-\cdot})$ are 12 and 17%, while that to $\phi_{11}(NA^{-\cdot})$ is 46%. This is caused by a strong coupling of the vacant NO_2 orbital with $\phi_8(A^{-\cdot})$. As a result, transition bands with quite different character appear in the spectrum of $NA^{-\cdot}$. The first four transitions are represented as follows:

$$\Psi_{I}(NA^{-\cdot}) = (0.52)^{1/2}\Phi_{10-11} + (0.32)^{1/2}\Phi_{9-11} + \cdots$$
$$\Psi_{II}(NA^{-\cdot}) = (0.62)^{1/2}\Phi_{10-12} + (0.20)^{1/2}\Phi_{10-13} + \cdots$$
$$\Psi_{III}(NA^{-\cdot}) = (0.51)^{1/2}\Phi_{9-10} + (0.20)^{1/2}\Phi_{10-11} + \cdots$$
$$\Psi_{IV}(NA^{-\cdot}) = (0.60)^{1/2}\Phi_{10-13} + (0.12)^{1/2}\Phi_{10-12} + \cdots .$$

Therefore I and III transition bands have the character of charge transfer state from anthracene to the nitro group.

The SCF MO diagram of $AA^{+\cdot}$ and $A^{+\cdot}$ is shown in Fig. 9. As in the case of $CA^{-\cdot}$, MO's of $AA^{+\cdot}$ are well correlated with those of $A^{+\cdot}$. Contributions of amino group to MO's of $AA^{+\cdot}$, ϕ_6—ϕ_9, are less than 11%. It should be noticed that the energy increase of $\phi_7(A^{+\cdot})$ is larger than those of other MO's($A^{+\cdot}$). Therefore, to a first approximation, energies of configurations $\Phi_{5-7}(A^{+\cdot})$ and $\Phi_{6-7}(A^{+\cdot})$ increase while that of $\Phi_{7-8}(A^{+\cdot})$ decreases. The MO's shown in Fig. 9 are related to first three transitions of $AA^{+\cdot}$ and $A^{+\cdot}$ as follows:

$$\Psi_{I}(A^{+\cdot}) = (0.89)^{1/2}\Phi_{5-7} + \cdots \qquad (^2B_{1g} \leftarrow {}^2B_{2g})$$
$$\Psi_{II}(A^{+\cdot}) = (0.87)^{1/2}\Phi_{6-7} + \cdots \qquad (^2A_u \leftarrow {}^2B_{2g})$$
$$\Psi_{III}(A^{+\cdot}) = (0.75)^{1/2}\Phi_{7-8} + \cdots \qquad (^2B_{3u} \leftarrow {}^2B_{2g})$$

$$\Psi_{\mathrm{I}}(\mathrm{AA}^{+\cdot}) = (0.66)^{1/2}\Phi_{8-9} + \cdots$$

$$\Psi_{\mathrm{II}}(\mathrm{AA}^{+\cdot}) = (0.61)^{1/2}\Phi_{6-8} - (0.26)^{1/2}\Phi_{7-8} + \cdots$$

$$\Psi_{\mathrm{III}}(\mathrm{AA}^{+\cdot}) = (0.58)^{1/2}\Phi_{7-8} + (0.27)^{1/2}\Phi_{6-8} + \cdots.$$

Therefore I and II transition bands of $\mathrm{A}^{+\cdot}$ shift to blue while III to red on amino group substitution. As a result these transition bands overlap one another. This situation can be understood by the resolved spectra of $\mathrm{AA}^{+\cdot}$.

Conclusion

Radical anions and cations of 9-methyl-, 9-bromo-, 9-cyano-, and 9-nitroanthracene have been prepared by γ-irradiation of the PVA–BuA and PVC–BuCl systems of their parent compounds. Cations of 9-aminoanthracene have also been prepared in the PVC–BuCl system. The stretched film technique combined with γ-irradiation has been applied to these radical ions. Resolved spectra have been obtained by analyzing the polarized absorption spectra quantitatively.

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References

1) H. Hiratsuka and Y. Tanizaki, *J. Phys. Chem.*, **83**, 2501 (1979).

2) K. Sekiguchi, H. Hiratsuka, Y. Hatano, and Y. Tanizaki, *J. Phys. Chem.*, **84**, 452 (1980).

3) J. Meisenheimer and E. Connerade, *Ann. Chem.*, **330**, 165 (1903).

4) R. Zahradnik and P. Carsky, *J. Phys. Chem.*, **74**, 1235 (1970).

5) A. Ishitani and S. Nagakura, *Theor. Chim. Acta*, **4**, 236 (1966).

6) J. W. Dodd, *J. Chem. Soc.*, *B*, **1971**, 2427.

7) T. Matsuyama and H. Yamaoka, *Annu. Rep. Res. React. Inst. Kyoto Univ.*, **7**, 29 (1974).

8) B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, **65**, 2588 (1969).

9) I. M. Panayotov and Ch. B. Tsvetanov, *Monatsh. Chem.*, **101**, 1672 (1970).

10) Y. Tanizaki and S. Kubodera, *J. Mol. Spectrosc.*, **24**, 1 (1967); Y. Tanizaki, T. Yoshinaga, and H. Hiratsuka, *Spectrochim. Acta, Part A*, **34**, 205 (1978).

11) L. Margulies and A. Yogev, *Chem. Phys.*, **27**, 89 (1978).

12) E. W. Thulstrup, J. Michl, and J. H. Eggars, *J. Phys. Chem.*, **74**, 3808 (1970).