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Stabilization Energy of the 9,9′-Trimethylenedianthracene Radical Cation Estimated by the Charge Resonance Band

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Synopsis. The charge-resonance band of the 9,9′-trimethylenedianthracene radical cation (9An9An$^{\dot{+}}$) was observed at 1550 nm by laser photolysis in the near-IR region. Two anthracene chromophores of 9An9An$^{\dot{+}}$ were found to take a full-overlap conformation; a clear relationship between the dimer stabilization energy and the aromatic ring size was shown.

Dimer radical cation formation of aromatic molecules have been extensively studied using ESR,[1] γ-ray irradiation in low-temperature rigid matrices,[2,3] pulse radiolysis,[4,5] and laser photolysis.[6,7] The properties of these dimer radical cations are important to understand the polymerization mechanisms,[8] and the neighboring interaction of radical ions formed in polymer systems.[9,10] Recently, we have studied the charge-resonance (CR) band of intramolecular bichromophoric compounds in order to estimate the stabilization energy of dimer radical cation formation.[11] So far, aromatic chromophores carbazole,[11] naphthalene,[10] and pyrene[12] have been studied. In this wotk, the CR band absorption of 9,9′-trimethylenedianthracene (9An9An) was measured by the near-IR laser photolysis. The aims of this study were: (1) to determine the stabilization energy of the anthracene dimeric radical cation at a limited conformation of the intramolecular system, and (2) to obtain the CR band absorption which excludes participation of the partial overlap dimeric radical cation.

Experimental

9,9′-Trimethylenedianthracene (9An9An) was synthesized from anthrone and 1,3-dibromopropane.[13] Purification was achieved by silica-gel column chromatography and recrystallization. 9-Methylathracene (9MeAn, Aldrich), as a monomer model compound of 9An9An, and 1,2-Dicyanobenzene (DCNB, Wako Pure Chem. Ind.), as an electron acceptor, were purified by recrystallization. Acetonitrile (MeCN, Wako), the solvent for laser photolysis measurements, was refluxed over P_2O_5 several times and was then fractionally distilled.

All samples for optical measurements were degassed in a Pyrex ampule fitted with a 1-cm quartz cell.[12] Laser photolysis measurements were carried out by a Lambda Physik EMG101MSC excimer laser as a pulse source (ca. 20 ns fwhm, 351 nm, 60 mJ). Appropriate filters for laser pulses were used so as to avoid multiphotonic excitation of the samples. Measurements were made at 298 K; the details of the apparatus are given elsewhere.[12]

Results and Discussion

Figure 1 (left) shows the molecular structure of 9An9An studied in this work. When two anthracene chromophores are linked by a trimethylene chain, the sandwich conformation is expected to be formed in the cationic state, as shown in Fig. 1 (right).[14] For an intermolecular system, both chromophores of the dimer radical cation can take the conformation most preferable to increase the stabilization energy; in the intramolecular system, however, the overlap alignment of two chromophores is limited by the linkage of the trimethylene chain. On the other hand, the anthracene chromophore of 9An9An has another merit of molecular symmetry. As previously reported,[7,10] 1- and 2-naphthyl chromophores linked by a trimethylene chain can form two rotamers in a sandwich conformation, since these chromophores are not symmetric with respect to the substitution axes. However, the 9-substituted anthracene chromophore is symmetric and, hence, conformation of the determined dimeric radical cation is unique.

Laser photolysis measurements of 9MeAn (3.4×10^{-4} mol dm^{-3} with DCNB 5.0×10^{-2} mol dm^{-3} as an electron acceptor) in MeCN solvent gave the absorption bands of 9MeAn$^{\dot{+}}$ at 430 and 690 nm. The absorption band of 9MeAn triplet state was also observed at 430 nm. These band positions are in agreement with those reported in the literature.[3,15] At this low concentration of 9MeAn there was no absorption in the near-IR region due to intermolecular dimer radical cation formation.

The emission lifetime of the 9An9An singlet state was 7.2 ns in MeCN at 298 K; this state was quenched by DCNB with a diffusion-controlled rate constant. Figure 2 shows the transient absorption spectrum of 9An9An (1.5×10^{-4} mol dm^{-3}) in the presence of DCNB. At this low concentration of 9An9An, the intermolecular interaction is considered to be negligible. In Fig. 2, three absorption bands are recognized at 1550, 700, and

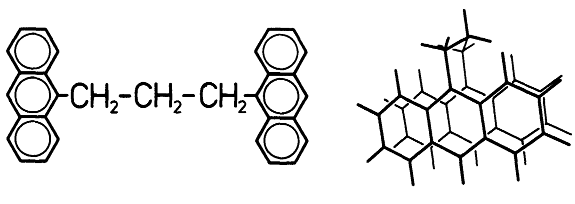

Fig. 1. Molecular structure of 9An9An (left) with a full overlap conformation (right).

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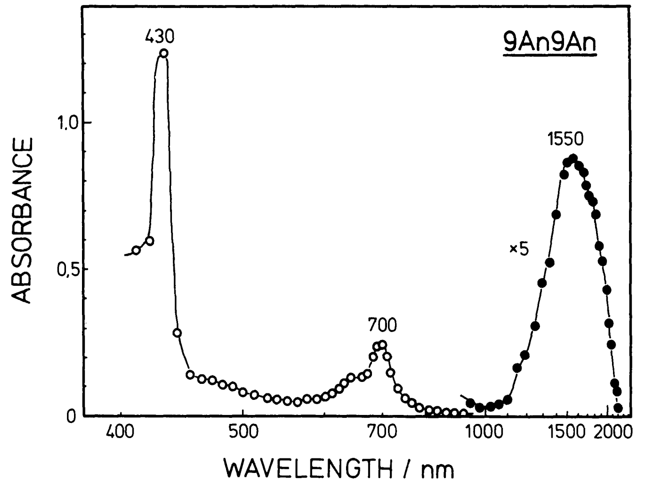

Fig. 2. Transient absorption spectrum at 500 ns after excitation for 9An9An (1.5×10^{-4} mol dm^{-3}) in the presence of DCNB (5.0×10^{-2} mol dm^{-3}). Measurements were made by a 351-nm laser pulse excitation in MeCN at 298 K.

430 nm. The 1550-nm absorption band, which did not exist in the spectrum of 9MeAn$^{+\cdot}$, is ascribed to the CR band of the 9An9An$^{+\cdot}$ dimeric radical cation. A high local concentration of anthracene in the intramolecular system promotes the dimeric radical cation formation, whose conformation is shown in Fig. 1 (right). The majority of 9An9An$^{+\cdot}$ is expected to form a sandwich dimeric radical cation in consideration of the results for other intramolecular bichromophoric C_3 compounds.[10,11,12)] Therefore, the bands at 700 and 430 nm are ascribed to the locally-excited bands of 9An9An$^{+\cdot}$: The absorption of the 9An9An triplet state also overlaps at 430 nm. The visible spectrum of 9An9An$^{+\cdot}$ resembles that of 9MeAn$^{+\cdot}$, which indicates a weak interaction, as was shown for the anthracene dimer radical anion.[16)]

The aromatic dimer radical cation shows the CR band in the near-IR region.[2)] The position of this band is a measure of the dimer radical cation stabilization.[17)] The relationship between the ring size of aromatic hydrocarbons and the position of the CR bands has already been discussed for a γ-ray irradiated system in a rigid matrix.[3)] The CR band positions for larger aromatic molecules shift to a longer wavelength, indicating the larger repulsive energy of the overlapping ring. The CR-band data for intermolecular naphthalene, anthracene, and pyrene taken from reference[3)] are shown in Table 1, with those measured for intramolecular bichromophoric compounds by laser photolysis at 298 K.[10,12)] Table 1 shows that the order of the stabilization energy for intramolecular compounds is in good agreement with the order of aromatic ring size, where the overlap conformation is fixed by the linkage of the trimethylene chain.

Table 1. Peaks and Half-Intensity Widths of CR Bands

Chromophore	γ-Ray at 77 K$^{a)}$ Peak	Width	Laser at 298 K Peak	Width
	μm^{-1}	μm^{-1}	μm^{-1}	μm^{-1}
Naphthalene	0.97	0.23	0.74$^{b,d)}$ 0.80$^{b,e)}$	0.35$^{b,d)}$ 0.41$^{b,e)}$
Anthracene	0.67	0.19	0.65	0.26
Pyrene	0.74	0.15	0.63$^{c,f)}$ 0.63$^{c,g)}$	0.24$^{c,f)}$ 0.26$^{c,g)}$

a) Ref. 3. b) Ref. 10. c) Ref. 12. d) 1,1′-Trimethylenedinaphthalene. e) 2,2′-Trimethylenedinaphthalene. f) 1,1′-Trimethylenedipyrene. g) 2,2′-Trimethylenedipyrene.

The measured CR band widths are also shown in Table 1. The halfwidths of the CR bands measured by γ-ray irradiation at 77 K were found to be ca. 0.2 μm^{-1} for condensed aromatic hydrocarbons.[3)] The obtained values for dinaphthylalkanes by laser photolysis are much larger than those for 9An9An and dipyrenylalkanes due to the overlap of two (full and partial) CR bands.[7,10)] The reasonable value for 9An9An shows the unique formation of a sandwich dimeric radical cation.

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