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Formation of σ- and π-Type Dimer Radical Cations by the Photochemical One-Electron Oxidation of Aromatic Sulfides

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Abstract: The formation of dimer radical cations from aromatic sulfides has been studied by photochemical one-electron oxidation in acetonitrile. When dicyanonaphthalene and thioanisole in acetonitrile were irradiated with nanosecond laser flash (308 nm), two types of dimer radical cations were detected at 470 and 800 nm at the expense of the monomer radical cation (520 nm). The intramolecular formation of similar radical ion complexes was observed for the cases of 1,n-bis(phenylthio)alkanes with $n = 3$ and 4, while bissulfides with $n = 2$, 6, and 8 showed radical cation spectra quite different from the above cases of $n = 3$ and 4. These facts indicate that dimer radical cations absorbing at around 460−500 nm are assigned as the σ-type complex of the sulfur−sulfur three-electron bond and that radical cations absorbing at around 800 nm are of the π-type complex associated with two phenylthio groups. For the case of *p*-methylthioanisole the formation of π-type dimer was shown to be reduced owing to the steric hindrance of two methyl groups. No formation of dimer radical cations was observed for cases of *p*-methoxythioanisole and diphenyl sulfide where the corresponding monomer radical cations are stabilized by the delocalization of positive charge on the sulfur atom. The density functional BLYP/6-31G* calculations on thioanisole predicted the existence of σ- and π-type dimer radical cations, in accordance with the experimental observation of approximately equal stability.

Introduction

Organic radical cations are important intermediates in photochemical electron-transfer reactions, with attention being focused on their structures and reactivities.[1] In reactions involving photoinduced electron transfers, some radical cations are known to form dimer radical cations by association with neutral, grand-state molecules. For example, dimer radical cations of aromatic hydrocarbons have been shown to play an important role in the back electron transfers taking place within geminate ion pairs formed upon photoinduced electron transfers.[2,3] Such dimer radical cations are divided into two types. One group of dimer radical cations is known as the π-type, in which the radical cations are stabilized by the charge resonance π-interaction with the neutral parent molecule.[2−6] These π-type dimers are also investigated as the simplest unit of π-stacked systems in examining the transannular interactions, which are important in numerous chemical and biological processes.[5] Another type of dimer radical cation, known as the σ-type, has a σ-bond with the neutral parent.[7−10] For example, the one-electron oxidation of aromatic olefines led to the formation of 1,4-distonic dimer radical cations.[8] An interesting structural change of the dimer radical cation of *trans*-stilbene was reported as the conversion of a face-to-face π-type dimer to the C−C bonded σ-type dimer.[6]

Asmus et al. have demonstrated that the radical cations of aliphatic sulfides are stabilized by forming the sulfur−sulfur two-center three-electron bonded (i.e., σ-type) dimers.[9] The

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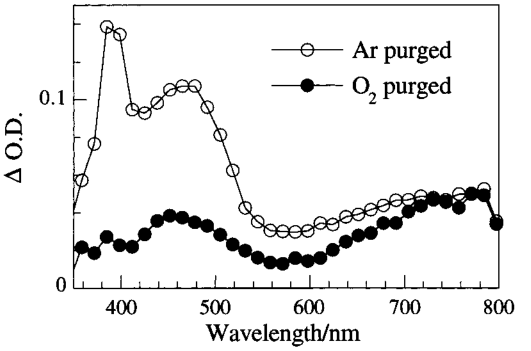
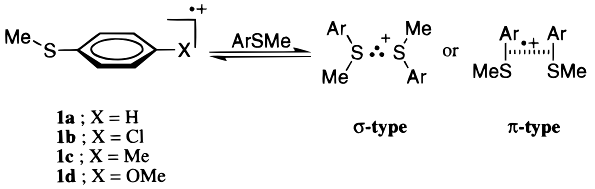


Figure 1. Transient absorption spectra under argon and oxygen observed at 100 ns after the laser excitation of acetonitrile solutions of 0.25 mM DCN and 100 mM thioanisole (**1a**). Open circles: argon atmosphere; solid circles: oxygen atmosphere.

Scheme 1



nature of such 2c-3e S∴S bonds has attracted considerable interest as possible intermediates in many enzymatic oxidations of organic sulfides.[10] Aromatic sulfides, which have an aromatic ring and sulfur atom, are interested in terms of types of dimers, i.e., a possible conformational switching between σ- and π-type dimers is expected. However, radical cations of aromatic sulfides[11] have been believed not to form any dimers because of the delocalization of positive charge/spin density over the aromatic rings. We have investigated radical cations of thioanisoles by laser flash spectrophotometry and illustrate here that both the σ- and π-type dimers could be formed depending on their substituents and concentrations (Scheme 1).

Results

Photosensitized One-Electron Oxidation of Thioanisole (1a). The pulsed laser excitation (XeCl, 308 nm, 10 ns) of 0.2 mM 1,4-dicyanonaphthalene (DCN) in the presence of 100 mM thioanisole (**1a**) in argon-saturated acetonitrile led to the quenching of the DCN fluorescence, and the production of transient species was observed by the absorption spectra. The spectrum 1 μs after the laser excitation showed the radical anion $DCN^{-\bullet}$ ($\lambda_{max} = 390$ nm), the excited triplet $^3DCN^*$ ($\lambda_{max} = 470$ nm),[12] and other transients ($\lambda_{max} = 470$ and 800 nm), and all of these (Figure 1; open circles) disappeared within a few microseconds. Here, $DCN^{-\bullet}$ and $^3DCN^*$ would be generated by the electron-transfer and substrate-enhanced intersystem crossing,[13] respectively, of excited singlet $^1DCN^*$. Interestingly, the typical absorption of thioanisole radical cation $\mathbf{1a}^{+\bullet}$ at 520 nm[11a] could not be observed under these conditions.

Under an oxygen atmosphere, the absorption of $DCN^{-\bullet}$ and $^3DCN^*$ decayed quite rapidly by the secondary electron transfer and energy transfer toward oxygen to form $O_2^{-\bullet}$ and $^1O_2$, respectively, while the species with $\lambda_{max} = 470$ and 800 nm were practically unaffected by the presence of oxygen (Figure 1; solid circles). Furthermore, when 0.2−0.4 mM perylene which has a lower oxidation potential (0.85 V vs SCE)[14] than **1a** (1.2 V vs SCE),[15] was added into the solution containing 100 mM **1a** and 0.2 mM DCN, the intermediate species decayed quite rapidly (1.3×10^{10} $M^{-1}s^{-1}$) with the concomitant growth in the absorption at 540 nm (perylene radical cation).[16] This observation is consistent with a diffusion-controlled hole-transfer from the intermediate to perylene, allowing the assignment as the radical cation species. It is apparent that the radical cation species are formed by the one-electron oxidation of **1a** and are different from the monomer radical cation $\mathbf{1a}^{+\bullet}$.

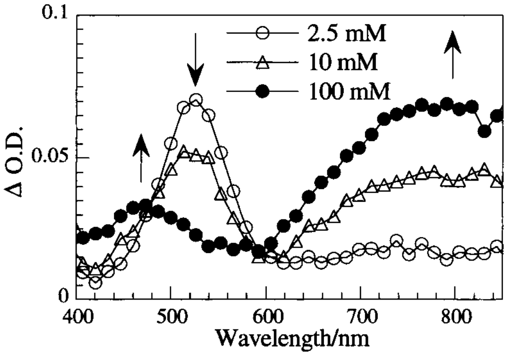


Figure 2. Effect of concentrations of **1a** on the transient absorption spectra. Observed at 1 μs after the laser excitation of oxygen-saturated acetonitrile solutions of 0.25 mM DCN, 100 mM BP, and 2.5−100 mM **1a**.

Effect of Concentration of Thioanisole (1a). The dependence on concentration (1 to 100 mM) of **1a** was examined for the photooxidation in the presence of 0.25 mM DCN and 100 mM biphenyl (BP). At the lower concentrations of **1a** the quenching of singlet $^1DCN^*$ by **1a** was insufficient because of the short lifetime of $^1DCN^*$ ($\tau_s = 10.1$ ns),[14] and hence BP (the oxidation potential of 2.0 V vs SCE)[14] was added as a hole mediator to quench $^1DCN^*$ efficiently. The pulsed laser excitation of DCN (0.25 mM) in the presence of 1 mM **1a** and 100 mM BP led to the production of transient absorptions due to $DCN^{-\bullet}$, $BP^{+\bullet}$ ($\lambda_{max} = 670$ nm),[17] and $^3DCN^*$, affording monomer radical cation $\mathbf{1a}^{+\bullet}$ ($\lambda_{max} = 520$ nm) by the diffusion-controlled hole transfer from $BP^{+\bullet}$ to **1a**. The spectra of $\mathbf{1a}^{+\bullet}$ were observed likewise under an oxygen atmosphere.

The concentration dependence of the transient absorption spectra is shown in Figure 2. The appearance of new absorption bands at 470 and 800 nm was observed as the concentration of **1a** was increased. The absorption of the latter species increased with increasing concentrations of **1a** at the expense of the absorbance of $\mathbf{1a}^{+\bullet}$; the decay kinetics of $\mathbf{1a}^{+\bullet}$ (520 nm) and of the other radical cation species (470 and 800 nm) were identical. These results clearly show that radical cation $\mathbf{1a}^{+\bullet}$ is in rapid equilibrium with the other radical cation species, i.e., dimer radical cation ($D^{+\bullet}$). A similar result was obtained when 9-cyanoanthracene (CA) was used in place of DCN as an electron acceptor.

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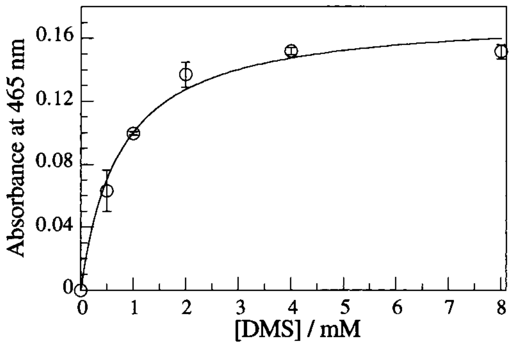

Figure 3. Plots of the absorbance of $(DMS)_2^{+\bullet}$ at 465 nm against the concentrations of DMS; the absorbance was obtained after the 308 nm laser flash photolyses of 0.2 mM DCN, 100 mM BP, and 0−8 mM DMS in oxygen-saturated acetonitrile.

The extinction coefficients of $\mathbf{1a}^{+\bullet}$ and $D^{+\bullet}$ could be estimated by Farid's hole transfer method (see Experimental Section).[17] Thus, values for the extinction coefficient of $\mathbf{1a}^{+\bullet}$ of $(6.1 \pm 0.3) \times 10^3\ M^{-1}\ cm^{-1}$ at 520 nm and that of $D^{+\bullet}$ of $(1.0 \pm 0.1) \times 10^4\ M^{-1}\ cm^{-1}$ at 800 nm were obtained. From these values, the equilibrium constant of eq 1 was estimated as described below. The pulsed laser excitation of 0.2 mM DCN was carried out in the presence of **1a** (2−16 mM) and 100 mM BP; under these conditions $BP^{+\bullet}$ is formed predominantly by the quenching of $^1DCN^*$, and the major portion of radical cation species, $\mathbf{1a}^{+\bullet}$ and $D^{+\bullet}$, is to be generated by the hole-transfer from $BP^{+\bullet}$. That is, the sum of quantum yields for formation of $\mathbf{1a}^{+\bullet}$ and $D^{+\bullet}$ was assumed to be constant.[2,3] Concentrations of each radical cation were calculated from the observed absorbances at 520 and 800 nm.[18] Then, we calculated the equilibrium constant (K) according to eq 2 for each concentration (2, 4, 8, and 16 mM) of **1a**. The resulting equilibrium constant was $(1.0 \pm 0.3) \times 10^2\ M^{-1}$ in acetonitrile. This value is much smaller than the reported value of $(6.2 \pm 0.4) \times 10^3\ M^{-1}$ for dimethyl sulfide (Me_2S; DMS) in water.[19] For comparison, the equilibrium constant of DMS was determined in acetonitrile in the presence of 0.5−8 mM DMS (for details, see the Experimental Section). The equilibrium constant (K_{DMS}) is given as follows:

$$\underset{\mathbf{1a}^{\bullet+}}{ArSMe^{+\bullet}} + \underset{\mathbf{1a}}{ArSMe} \xrightleftharpoons{K} \underset{\mathbf{D}^{\bullet+}}{(ArSMe)_2^{+\bullet}} \qquad (1)$$

$$K = \frac{[D^{\bullet+}]}{[\mathbf{1a}]\times[\mathbf{1a}^{\bullet+}]} \qquad (2)$$

$$K_{DMS} = \frac{[(DMS)_2^{\bullet+}]}{[DMS]\times[DMS^{\bullet+}]} \qquad (3)$$

The intensities of the absorptions of the dimer radical cation ($(DMS)_2^{+\bullet}$; $\lambda_{max} = 465$ nm)[20] were measured and plotted as a function of the concentration of DMS. The K_{DMS} value obtained by computation fitting was $(1.3 \pm 0.2) \times 10^3\ M^{-1}$ in acetonitrile (Figure 3). This result clearly indicates that the formation of the dimer radical cation of aryl sulfide **1a** is significantly inefficient, only one-tenth, in comparison to that of DMS.

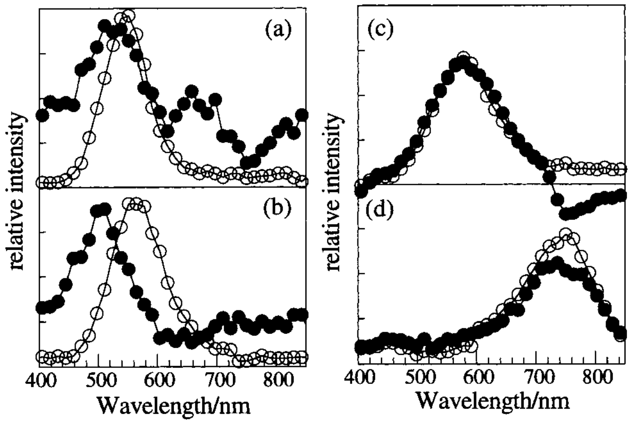

Figure 4. Transient absorption spectra for substituted thioanisole (**1b**−**d**) and diphenyl sulfide (**2**). Observed at 1 μs after the laser excitation of oxygen-saturated acetonitrile solutions. Open circles: 0.2 mM DCN, 0.1 M BP, 1 mM sulfides; solid circles: 0.2 mM 9-cyanoanthracene, 100 mM sulfides; (a) **1b**, (b) **1c**, (c) **1d**, and (d) **2**.

Radical Cation of Other Aromatic Sulfides. Other aromatic sulfides were likewise investigated in oxygen-saturated acetonitrile. For the cases of *p*-chloro- (**1b**) and *p*-methylthioanisole (**1c**), the pulsed laser excitation of 0.25 mM DCN, 1 mM sulfide, and 100 mM BP led to the production of transient absorption spectra due to sulfide monomer radical cations (i.e., $\mathbf{1b}^{+\bullet}$ and $\mathbf{1c}^{+\bullet}$), as reported,[15] 1 μs after the laser excitation (Figure 4a,b; open circles). When the irradiation was performed in the presence of 100 mM sulfide,[21] quite different spectra were obtained upon the excitation (Nd:YAG, 355 nm, 10 ns) of 0.2 mM CA (Figure 4a,b; solid circles). The resulting spectra showed the absorption bands at 520, 670, and >800 nm (broad band) for **1b** and 500 and >700 nm (broad band) for **1c**. Since these absorptions increased with the increasing concentration of sulfide, it is reasonable to suppose that the spectra are due to the dimer radical cations such as $D^{+\bullet}$.

In the cases of *p*-methoxythioanisole (**1d**) and diphenyl sulfide (**2**), the spectral shapes of monomer radical cations remained unaffected even when the sulfide concentrations were increased up to 100 mM (Figure 4c,d). These results show that no dimer radical cation is formed from sulfide **1d** and **2**.

Radical Cation of Aromatic Bissulfides. The radical cations of aromatic sulfides are expected to form two types of dimer radical cations. As described above, photooxidation of **1a** shows two kinds of absorption bands at 470 and 800 nm. Then, we examined the photooxidation of related aromatic bissulfides to clarify what types of dimers are formed from aromatic sulfides.

Asmus et al. reported that the one-electron oxidation of aliphatic bissulfides ($MeS(CH_2)_nSMe$; $n = 2−6$) led to the production of absorption spectra of intramolecular σ-type radical cations, which showed similar spectra with maximum absorptions varying with the number of methylene chains.[9,22] We carried out the one-electron oxidation of 1,*n*-bis(phenylthio)-alkanes ($(PhS(CH_2)_nSPh$; $n = 2, 3, 4, 6$, and 8) (**3a**−**e**) and examined the methylene chain effect on the corresponding cation radicals. The photooxidation of 1 mM **3a**−**e** in the presence of 0.25 mM DCN and 100 mM BP led to the production of transient spectra of their radical cations (Figure 5). Radical cations of **3b** and **3c** ($n = 3$ and 4, respectively) showed spectra

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(18) The dimer radical cation ($D^{\bullet+}$) absorbs at 520 nm as well as at 800 nm, while the monomer radical cation ($\mathbf{1a}^{\bullet+}$) does not absorb at 800 nm. Thus, the concentration of $D^{\bullet+}$ was determined from the absorbance at 800 nm, and then the concentration of $\mathbf{1a}^{\bullet+}$ was determined after correction by subtracting the absorbance of $D^{\bullet+}$ at 520 nm.

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(21) These sulfides (**1b** and **1c**) have a weak absorption band at 308 nm, then we use CA as a electron-accepting sensitizer to avoid direct irradiation of sulfides.

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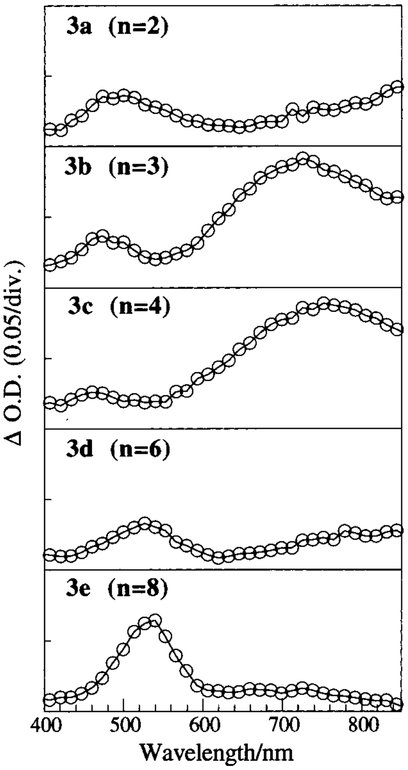

Figure 5. Transient absorption spectra observed at 1 μs after the laser excitation of oxygen-saturated acetonitrile solutions of 0.25 mM DCN and 1 mM bis(phenylthio)alkanes (**3a**−**e**); n = number of methylenes.

similar to that of **1a**. On the other hand, spectra of **3a** ($n = 2$) and **3d** ($n = 6$) had two peaks absorbing around 500 nm and >800 nm (the λ_{max} of the latter absorption band could not be observed in our observation window). In the case of **3e** ($n = 8$), the spectrum of the cation radical resembles that of monomer radical cation $\mathbf{1a}^{+\bullet}$, suggesting no formation of intramolecular dimer complex. It is interesting to note that the absorption band at around 800 nm was observed only for the cases of $n = 3$ and 4, whereas the absorption at around 500 nm was observed in almost all cases. The λ_{max} values of the shorter absorption bands varied between 470 and 530 nm depending on the number of methylenes. The shortest λ_{max} value was observed with the three-methylene compound ($n = 3$), in analogy with the reported case of aliphatic bissulfides, reflecting the overlapping interacting of p orbitals of two sulfur atoms.

A somewhat different result was obtained from the one-electron oxidation of 1,3-bis[*p*-(methylthio)phenyl]propane (**4**). Absorption maxima appeared at 580 and over 850 nm (Figure 6), and $\mathbf{4}^{+\bullet}$ has no absorption in the 400−500 nm region.

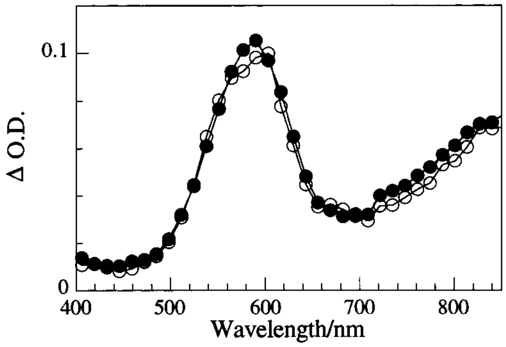

Figure 6. Transient absorption spectra observed at 1 μs after the laser excitation of oxygen-saturated acetonitrile solutions of 0.2 mM DCN, 100 mM biphenyl, and bissulfide **4**. Open circles: 0.2 mM **4**; solid circles: 1.0 mM **4**.

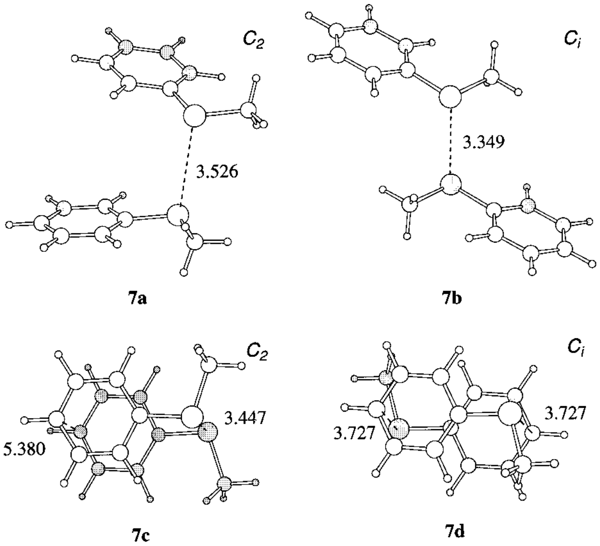

Figure 7. BLYP/6-31G* optimized geometries for dimer radical cations from **1a**; the σ-type dimer radical cations (**7a**,**b**) and the π-type dimer radical cations (**7c**,**d**). Distances are in angstroms.

Theoretical Study. Calculations of the geometries and bond enthalpies of dimers $D^{+\bullet}$ were performed at the BLYP/6-31G* level.[7e,9b] Structures of the dimeric species between the neutral and the radical cation are shown in Figure 7 and the resulting potential energy surface is shown in Figure 8. The optimized geometrical parameters of C_2 or C_i structures for **7a**−**d**[23] are shown here. Four structures were predicted as the dimer radical cations of **1a** in the saddles of the potential energy surface, i.e., two sulfur-associated structures (**7a**,**b**) and two phenylthio-associated ones (**7c**,**d**). While two phenyl groups are leaved in the former case, phenylthio groups overlap each other in the latter. The intermolecular S−S distances are 3.526, 3.349, and 3.447 Å, for **7a**−**c**, respectively, and the distance between S and C at the 4-position is 3.727 Å for **7d**. Their bond enthalpies are −21.3, −21.6, −21.0, and −19.9 kcal/mol for **7a**−**d**, respectively. The difference in enthalpies are quite small.

Discussion

Formation of Dimer Radical Cations of 1a. Dimer radical cations of thioanisoles are shown to be formed by the photooxidation with electron-accepting sensitizers in acetonitrile.[24] The dimer radical cation of **1a** is in equilibrium with its monomer radical cation and neutral parent, and its equilibrium constant is much smaller than that of DMS. It has been believed that **1a** cannot form dimer radical cations, because of the delocalization of the positive charge, by pulse radiolysis studies in aqueous solutions. In this case, the solubilities of **1a** in water are much lower than that of DMS, and hence the dimer formation could not be observed from **1a**. The present result shows that the reason there is no observation of the dimer radical cation of **1a** is the poor solubility in water and the relatively small equilibrium constant. Recently, Mittal et al. have reported that

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(23) (a) Recently, Bally et al. reported about the incorrectness of the prediction of symmetric dimer radical ions in density functional calculations.[23b] Then, we calculated the geometries of dimer radical cations of **1a** without symmetrical restriction. However, their geometries and bond enthalpies were not so changed. (b) Bally, T.; Sastry, N. *J. Phys. Chem. A* **1997**, *101*, 7923−7925.

(24) Recently, H. D. Roth and coworkers also detected the σ-type dimer radical cation of thioanisole (**1a**) in zeolite by ESR. We thank Prof. Roth for private communication prior to publication.

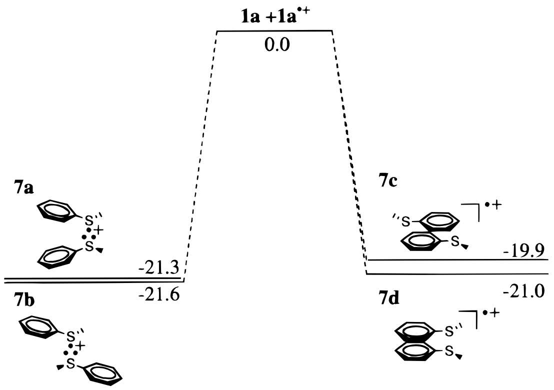


Figure 8. Potential energies for the formation of dimer radical cations from **1a** and **1a**$^{+\bullet}$ calculated at the BLYP/6-31G* level. The structures of the radical cation species are given in Figure 7 and the energies are given in kcal/mol.

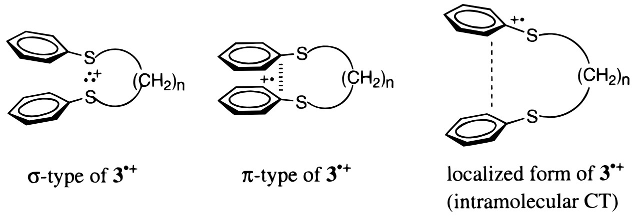
the dimer radical cation of **1a** absorbing at 410 nm was observed in aqueous solutions.[25] According to the present results, however, the concentration of **1a** was too low to observe their dimer radical cations. Then, the reported intermediate absorbing at 410 nm might be different from the dimer radical cation of **1a**.

While dimer radical cations were observed in the cases of **1a**−**c**, dimer cations were not observed from **1d** and **2**. These aromatic sulfides have a strong electron donating *p*-methoxyphenyl group and two phenyl groups, and hence the delocalization of positive charge over the aromatic rings is more effective than those in the other aromatic sulfides (**1a**−**c**). Thus, the formation of dimer radical cations is unfavorable and could not be observed for the cases of **1d** and **2**.

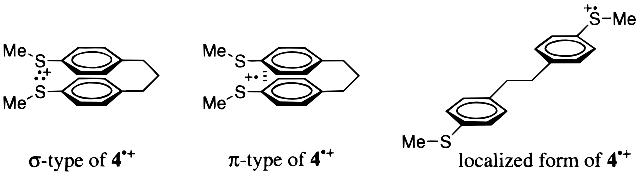
σ- and π-Type Dimer Radical Cations. Radical cations of aliphatic sulfides are known to form the σ-type dimer radical cations absorbing in the 450−550 nm region due to $\sigma-\sigma^*$ transition.[21a] For the case aromatic bissulfides (**3**) the π-type dimer radical cations are also expected. In fact, the radical cations of bissulfides **3a**−**d** showed absorption bands around the 470−530 and >700 nm regions (Figure 5). In addition, the absorption band of **3**$^{+\bullet}$ in the shorter wavelength region showed the methylene chain effect similar to the case of aliphatic bissulfides as reported by Asmus et al.[9,22] Thus, it may be concluded that absorption bands of **3a**−**d**$^{+\bullet}$ around the 470−530 nm region are due to the $\sigma-\sigma^*$ transition of the σ-type complex (or dimer radical cations) of aromatic sulfides. While the spectra of **3b**$^{+\bullet}$ and **3c**$^{+\bullet}$ resembled that of D$^{+\bullet}$ (dimer of **1a**$^{+\bullet}$), those of **3a**$^{+\bullet}$ and **3d**$^{+\bullet}$ showed the broad absorption band laying over 800 nm. This result indicates that the two phenylthio groups in **3a**$^{+\bullet}$ and **3d**$^{+\bullet}$ may not associate to form an intramolecular π-type radical cation complex because of the unfavored methylene chains.[26] It is suggested that the absorption band at $\lambda_{\max} = 700-750$ nm is due to the π-type dimer (or complex of) radical cations of aromatic sulfides. The broader peaks at >800 nm seem not to come from the π-type complex but from an intramolecular charge transfer (see Scheme 2).

The radical cation of **4** also has two types of absorption bands at 580 and over 850 nm. However, the absorption band at 580 nm is slightly longer than that of the $\sigma-\sigma^*$ transition of σ-type dimer radical cations and the shape of its spectrum resembles that of the monomer radical cation of **1c**$^{+\bullet}$. If the positive charge was localized in the sulfur atom and the σ-type radical cation complex of **4** with a cyclophane structure was formed, the unfavorable strain and electronic repulsion between the two neutral phenyl groups may be significant. Thus, the observed absorption band from **4**$^{+\bullet}$ was assigned to the localized form of **4**$^{+\bullet}$ as shown in Scheme 3. On the other hand, the π-type intramolecular complex of **4**$^{+\bullet}$ would be favorable because two phenylthio groups are combined by three methylene groups.[26] Thus, it may be concluded that the absorption band around 700−800 nm is due to the π-type complex of radical cations.

Scheme 2



Scheme 3



The radical cations of *p*-chloro- (**1b**) and *p*-methylthioanisoles (**1c**) also showed two types of dimer radical cations. In these cases, however, the absorptions of σ-type dimers of the shorter wavelength are much stronger than those of π-type dimers. This fact might indicate that the σ-type dimers are formed predominately because of the steric repulsion of para-substituent groups in forming π-type dimers.

Geometries and Bond Enthalpies of $(\mathbf{1a})_2^{+\bullet}$. Two σ-type and two π-type structures of dimer radical cations of **1a** are predicted to exist by theoretical calculations at the BLYP/6-31G* level (Figure 8). The intermolecular sulfur−sulfur distances of 3.35−3.53 Å for σ-type dimer radical cations are significantly longer than those of aliphatic sulfides (ca. 2.8 Å),[9b,27] and bond enthalpies of σ-type dimers (−21 to −22 kcal/mol) are smaller than those of aliphatic sulfides (−26 to −30 kcal/mol).[28] The smaller value of K (eq 1) for aromatic **1a** reflects the longer and weaker S−S σ-bond. The reason for the higher bond enthalpies for the case of **1a** is the fact that the monomer radical cation of **1a**$^{+\bullet}$ is stabilized by the delocalization of positive charge to the aromatic ring and hence the electrophilicity of the sulfur atom in **1a**$^{+\bullet}$ is weakened. On the other hand, the delocalized positive charge over the aromatic ring is stabilized by forming the π-type dimers by charge resonance between phenylthio groups (Figure 8; **7c**,**d**). Thus far, the formation of π-type dimer radical cations was reported for hydrocarbon aromatic compounds with various structures and ionization potentials,[29] the reported enthalpies being −16 to −24 kcal/mol.[29c] The calculated values for the π-type dimers of aromatic sulfide **1a** are in good agreement with these reported values.

It is worth noting that the difference in bond enthalpies between the σ- (**7a**,**b**) and π-types (**7c**,**d**) is quite small. This

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indicates that the relative contents of σ- and π-types of dimers do not differ much at the equilibrium condition (eq 4). If the enthalpy of one of the dimers is slightly varied by substituents, the equilibrium constant may be changed significantly. For the cases of **1b** and **1c**, the content of π-type dimer radical cations is shown to be much lower than that of σ-type dimers. Since the electronic effect of the *p*-chloro or the *p*-methyl substituent is not large, the instability of π-type dimers is caused by the steric repulsion of the substituent.

$$\mathbf{1}^{\bullet+} + \mathbf{1} \overset{K}{\rightleftharpoons} \boxed{\sigma\text{-}\mathbf{1}_2^{\bullet+} \rightleftharpoons \pi\text{-}\mathbf{1}_2^{\bullet+}} \qquad (4)$$

Conclusion

In the photochemical one-electron oxidation of aromatic sulfides (**1**), dimer radical cations are shown to be formed in rapid equilibrium with monomer radical cation $\mathbf{1}^{+\bullet}$. The complex formation of σ- and π-types is evidenced and shown to be sensitive to the steric and electronic influence of substituents. The competitive formation of σ- and π-type dimer radical cations indicates that the delocalization of positive charge on the sulfur atom is to reduce the tendency to make the σ-type three-electron S−S bond. The selective formation of σ- and π-type radical cation dimers may provide a novel switching of electronic structures of radical cation species.

Experimental Section

^{1}H NMR spectra were recorded with a Varian GEMINI-200 (200 MHz) NMR spectrometer. GC/MS analyses were carried out with a Shimadzu QP-5000 mass spectrometer, using a 0.2 mm × 25 m capillary column of CBP1-M50-025 (Shimadzu). GLC analyses were performed with a Shimadzu GC-14A gas chromatograph, using a 2.5 mm × 1 m column of Carbowax 300M, 2% on Chromosorb WAW (GL Sciences).

Materials. Acetonitrile was distilled from phosphorus pentoxide. 9-Cyanoanthracene (CA) received from Tokyo Kasei was recrystallized from ethanol. Thioanisole (**1a**), *p*-chloro- (**1b**) and *p*-methylthioanisole (**1c**), and diphenyl sulfide (**2**) were received from Tokyo Kasei and purified by distillations. *p*-Methoxythioanisol (**1d**) was received from Aldrich and distilled. 1,4-Dicyanonaphthalene (DCN),[30] 1,*n*-bis(phenylthio)methane (**3**; $n = 2-8$)[31] and 1,3-bis[*p*-(methylthio)phenyl]-propane (**4**)[32] were prepared according to the reported procedures.

Time-Resolved Absorption Spectroscopy. Laser kinetic spectroscopy experiments were carried out with a nanosecond laser system as described previously.[33] The system consisted of a 150 W Xe flash lamp (XF-80, Tokyo Instruments), a SPEX 270M monochromator, and a HAMAMATSU R-1221HA photomultiplier tube. The CCD detector (ICCD-1024-MLΔ*G*-E, Princeton Instruments) was controlled by a detector controller (ST-135, Princeton Instruments) and a pulse generator (PG-200, Princeton Instruments). The system was controlled by a PC-9801 computer that was interfaced (GPIB) to the detector controller. The delay time of this system was controlled by two digital delay/pulse generators (DG-535, Stanford Research system). The excitation source was a Physik MINex XeCl excimer laser (308 nm, ∼10 ns, ∼15 mJ/pulse) or the third harmonic (355 nm, ∼6 ns, ∼25 mJ/pulse) from a Spectron SL248G Nd:YAG laser. The oxygen-saturated sample solutions were irradiated in a 4 × 1 cm^2 cell made of quartz.

Determination of Extinction Coefficients of $\mathbf{1a}^{+\bullet}$ and $\mathbf{D}^{+\bullet}$. After the pulsed laser excitation of DCN in the presence of 1 mM **1a** and 100 mM biphenyl (BP) in acetonitrile, the decay in the absorption at 670 nm ($BP^{+\bullet}$) and the concomitant growth in absorption at 520 nm ($\mathbf{1a}^{+\bullet}$) due to the hole-transfer, in which the maximum concentration of $\mathbf{1a}^{+\bullet}$ was equal to that of the initially formed $BP^{+\bullet}$ was observed. By use of the extinction coefficient of $BP^{+\bullet}$ of 1.5×10^4 M^{-1} cm^{-1} at 670 nm,[16] that of $\mathbf{1a}^{+\bullet}$ of $(6.1 \pm 0.3) \times 10^3$ M^{-1} cm^{-1} at 520 nm was obtained from the signal intensities. This value is in good agreement with the reported value of 5×10^3 M^{-1} cm^{-1}.[10a] Similarly, an experiment performed in the presence of 0.3 mM DCN, 500 mM **1a**, and 0.4 mM perylene resulted in the decay in the absorption at 800 nm and the concomitant growth in the absorption at 540 nm (perylene$^{+\bullet}$; $\epsilon_{540} = 4.9 \times 10^4$ M^{-1} cm^{-1}). The extinction coefficient for $D^{+\bullet}$ was determined to be $(1.0 \pm 0.1) \times 10^4$ M^{-1} cm^{-1} at 800 nm.

Calculation of the Equilibrium Constant of $(\mathbf{DMS})_2^{+\bullet}$. The equilibrium constant (K_{DMS}) for dimer formation from $DMS^{+\bullet}$ (DMS = Me$_2$S) is given by eq 3. Although both $\mathbf{1a}^{+\bullet}$ and $D^{+\bullet}$ absorb in the region of VIS-near-IR, $DMS^{+\bullet}$ does not absorb in this region[19] and we can only observe the radical cation dimer ($(DMS)_2^{+\bullet}$; $\lambda_{max} = 465$ nm).[34] Under the present conditions, radical cation species, $DMS^{+\bullet}$ and $(DMS)_2^{+\bullet}$, are generated by the hole transfer from $BP^{+\bullet}$. It is reasonable to suppose that the sum of concentrations of radical cation species is equal to the initially formed $BP^{+\bullet}$ since the rate of hole transfer is fast and efficient. Thus, the concentration of $DMS^{+\bullet}$ can be represented as eq 5:

$$[DMS^{+\bullet}] = [(DMS)_2^{+\bullet}]_\infty - [(DMS)_2^{+\bullet}] \qquad (5)$$

where $[(DMS)_2^{+\bullet}]_\infty$ is the concentration of $(DMS)_2^{+\bullet}$ when all radical cation species converted to the dimer radical cation. From eqs 3 and 5, the concentration of $(DMS)_2^{+\bullet}$ is represented as a function of concentration of DMS (eq 6).

$$[(DMS)_2^{+\bullet}] = \frac{K_{DMS} \times [(DMS)_2^{+\bullet}]_\infty [DMS]}{1 + K_{DMS} \times [DMS]} \qquad (6)$$

Unfortunately, the extinction coefficient for $(DMS)_2^{+\bullet}$ in acetonitrile is not known. Since concentrations are proportional to their absorbances, the concentration of $(DMS)_2^{+\bullet}$ can be replaced by its absorbance. The absorbances at 465 nm were measured and plotted against the concentrations of DMS. Then, we simulated the absorbance curve by varying K_{DMS} values and the absorbance of $[(DMS)_2^{+\bullet}]_\infty$ as shown in Figure 3 and the equilibrium constant K_{DMS} was estimated to be $(1.3 \pm 0.2) \times 10^3$ M^{-1} in acetonitrile. Calculations of equilibrium constants of eq 6 and fittings to the experimental data (Figure 3) were carried out on an Apple Macintosh computer with the program IGOR PRO (Wavemetrics).

Calculations of Geometries of Radical Ion Species from 1a. Calculations of geometries and bond enthalpies of the radical cation dimer ($D^{+\bullet}$) were performed at the BLYP/6-31G* level.[7e,9b] Calculations have been made by using the Turbomole version 95.0 in the Insight II program system. Geometries and potential energies of various dimer structures are shown in Figures 7 and 8. Detailed data are given in the Supporting Information.

Acknowledgment. We thanks Prof. Heinz H. D. Roth for helpful discussions. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture, and Sports of Japan. The computation was done at the CAD facility of Nagoya University Venture Business Laboratory.

Supporting Information Available: Cartesian coordinates (Å) for structures of **1a** and its radical cation species ($\mathbf{1a}^{+\bullet}$ and **7a−d**) at the BLYP/6-31G* level as well as its total energies (4 pages print/PDF). See any current masthead page for ordering information and Web access instructions.

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