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UV Photolysis of 1,4-Diaminobenzene in a Low-Temperature Argon Matrix to 2,5-Cyclohexadiene-1,4-diimine via 4-Aminoanilino Radical

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UV photolysis of 1,4-diaminobenzene isolated in a low-temperature argon matrix has been investigated by Fourier transform infrared spectroscopy with the aid of the density-functional-theory calculation. Infrared bands of an intermediate produced from 1,4-diaminobenzene upon UV irradiation ($\lambda < 350$ nm) are assigned to a semiquinone-type radical, 4-aminoanilino radical. A final product produced from the 4-aminoanilino radical upon shorter-wavelength irradiation ($\lambda < 310$ nm) is assigned as 2,5-cyclohexadiene-1,4-diimine. Optimized structures of 1,4-diaminobenzene, 4-aminoanilino radical, and 2,5-cyclohexadiene-1,4-diimine are compared with one another, resulting in changes of the π -conjugated system similar to those of the hydroquinone and 1,4-benzoquinone system. In addition, *trans*–*cis* isomerization of 2,5-cyclohexadiene-1,4-diimine upon UV irradiation is observed in photoequilibrium, where the *cis*/*trans* population ratio depends on the irradiation wavelength.

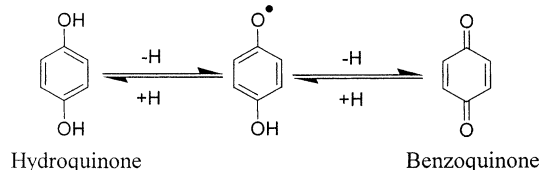
1. Introduction

The oxidation–reduction system between hydroquinone and 1,4-benzoquinone has attracted the attention of many researchers who study electron and/or proton transport in biological systems.¹ This oxidation–reduction system is applied to a quinhydrone electrode to measure proton concentration in solutions. A reaction intermediate between hydroquinone and benzoquinone was identified as *p*-benzosemiquinone radical, as shown in the Scheme 1.^{2–5} For example, Trinpathi and Schuler observed a time-resolved resonance Raman spectrum of transient species in the pulse radiolysis of hydroquinone solution and identified the observed spectrum of *p*-benzosemiquinone radical by a vibrational analysis.³ On the other hand, Jäger and Norris investigated laser flash photolysis of hydroquinone and benzoquinone by time-resolved electron spin resonance spectroscopy and detected the signals of the semiquinone radical.⁵

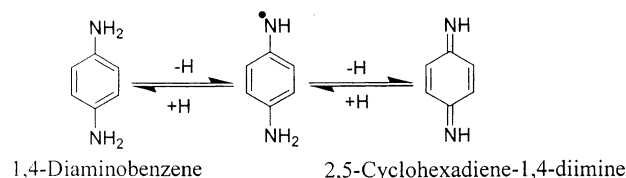
In the present study, we have investigated a similar oxidation–reduction system having a NH_2 group instead of a OH group, i.e., 1,4-diaminobenzene and 2,5-cyclohexadiene-1,4-diimine system. By analogy with the hydroquinone and benzoquinone system, 4-aminoanilino radical is expected to be a reaction intermediate produced from 1,4-diaminobenzene by dissociation of one hydrogen atom; another dissociation of one hydrogen atom of the other amino group produces a final product, 2,5-cyclohexadiene-1,4-diimine, where the π -conjugated system is quinone-type, as shown in Scheme 2.

Reports on the 1,4-diaminobenzene and 2,5-cyclohexadiene-1,4-diimine system are fewer than those on the hydroquinone and benzoquinone system, and the intermediate has not been identified so far, because the intermediate and the final product are both less stable than the corresponding species in the hydroquinone and benzoquinone system. Thus, the purposes of the present study are (i) to measure infrared spectra of the photoreaction intermediates and final products by the low-

SCHEME 1



SCHEME 2



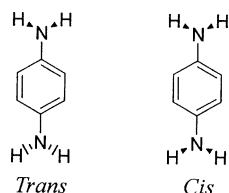
temperature matrix-isolation technique, (ii) to analyze the observed bands by comparison with the calculated spectral patterns obtained by the density-functional-theory (DFT) calculation, and (iii) to elucidate the photoreaction mechanism of the 1,4-diaminobenzene and 2,5-cyclohexadiene-1,4-diimine system. In the present study, we show the first experimental evidence for 4-aminoanilino radical, where the π -conjugated system is similar to that of *p*-benzosemiquinone radical.

2. Experimental and Calculations

Since the vapor pressure of 1,4-diaminobenzene, purchased from Tokyo Chemical Industry Co. Ltd., was too low to transfer the vapor sufficiently into a glass cylinder, a small amount of the solid was placed in a stainless steel pipe nozzle with a heating system, on which pure argon gas (Nippon Sanso, 99.9999% purity) was flowed. The sample was heated to about 310 K, and the flow rate of rare gas was adjusted by a needle valve to obtain sufficient isolation. The mixed gas was expanded through a stainless steel pipe (o.d. 1/16 in.) and deposited in a

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SCHEME 3



vacuum chamber on a CsI plate cooled by a closed-cycle helium refrigerator (CTI Cryogenics, model M-22) to about 16 K. The temperature of the CsI plate was controlled with a PID (proportional plus integral plus derivative) action method and changed at a rate of 1 K/min to anneal the matrix sample. UV/vis light from a super-high-pressure mercury lamp was used for photolysis of the sample. A water filter was used to remove thermal reactions, and UV-36, UV-34, UV-32, UV-30, and UV-28 short-wavelength cutoff filters and a U-330 band-path filter (HOYA) were used to select the irradiation wavelength. Infrared spectra of the matrix samples were measured with an FTIR spectrophotometer (JEOL, model JIR-7000). The spectral resolution was 0.5 cm^{-1} , and the accumulation number was 64. Other experimental details were reported elsewhere.^{6,7}

DFT calculations were performed using the GAUSSIAN 98 program⁸ with the 6-31++G** basis set. Becke's three-parameter hybrid density functional,⁹ in combination with the Lee–Yang–Parr correlation functional (B3LYP),¹⁰ was used to optimize the geometrical structures. The open shell model was used for the calculations of radicals.

3. Results and Discussion

3.1. Conformation of the Reactant 1,4-Diaminobenzene.

Since the reactant 1,4-diaminobenzene is stable under normal conditions, some spectroscopic data have been obtained in the solid and solution in addition to theoretical data at various calculation levels.^{11–15} There are two possible conformations for 1,4-diaminobenzene, as shown in Scheme 3; the two hydrogen atom pairs of the amino groups for the *trans* conformation are on opposite sides of the molecular plane, while those for the *cis* conformation are on the same side.

Whether both *trans* and *cis* conformations coexist has not been clarified. For example, Tzeng and Narayanan compared the experimental vibrational wavenumbers with the corresponding theoretical values obtained by the Hartree–Fock/6-31+G* method and temporarily assigned the observed bands to only the *trans* conformation.¹⁴ On the other hand, Akalin and Akyüz assumed in their normal-coordinate analysis of the infrared spectra that the *trans* and *cis* isomers exist in the solid.¹⁵ Thus, we first tried to distinguish the bands of each isomer, because infrared spectra of matrix-isolated species are usually composed of sharp bands with a bandwidth of a few cm^{-1} .

The energy difference between the more stable isomer, *trans*, and the less stable isomer, *cis*, has been calculated to be 0.28 kJ mol^{-1} by the present DFT calculation, while the isomerization barrier from *trans* to *cis* is 13.8 kJ mol^{-1} . Since the population ratio of the isomers at the deposition temperature is usually maintained in a low-temperature matrix,¹⁶ the *cis/trans* population ratio of 1,4-diaminobenzene in the matrix is estimated to be about 0.9, assuming the Boltzmann distribution law at 310 K. This means that infrared bands of the two isomers can be measured by the matrix-isolation technique, if the hydrogen atom tunneling does not occur, unlike for hydroquinone.¹⁷

The observed matrix infrared spectrum of 1,4-diaminobenzene is shown in Figure 1. The bandwidth of almost all the bands is

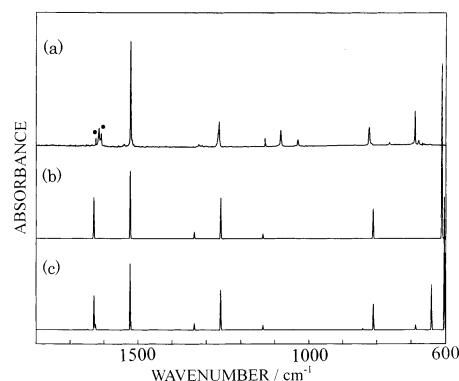


Figure 1. Infrared spectrum of 1,4-diaminobenzene in an argon matrix and calculated spectral pattern obtained by DFT/B3LYP/6-31++G**: (a) observed spectrum (bands marked with “●” are due to a small amount of water impurity); (b, c) calculated spectral patterns of the *trans* and *cis* isomers, respectively. A scaling factor of 0.98 is used.

about 1 cm^{-1} , which is much narrower than that previously observed in the solid and solution. To distinguish the *trans* and *cis* bands, we have also calculated the infrared spectral patterns of the two isomers by the DFT/B3LYP/6-31++G** method. As compared in Figure 1, the wavenumbers of the *trans* bands measured in the region between 800 and 1500 cm^{-1} are found to be consistent with the corresponding *cis* bands within 1 cm^{-1} . One possibility to distinguish the isomer bands is to examine the NH_2 scissoring mode around 1600 cm^{-1} , where one and two bands should appear for the *trans* and *cis* isomers, respectively. However, this spectral region is disturbed by a small amount of water impurity, and thus, it is difficult to find the second *cis* band. Another possibility to distinguish the isomer bands is to examine the NH_2 wagging mode around 600 cm^{-1} , where one and two bands for the *trans* and *cis* isomers, respectively, should appear as for the NH_2 scissoring mode. One strong band appearing at 688 cm^{-1} may be assigned to the second NH_2 wagging mode for the *cis* isomer, where the corresponding calculated value is 641 cm^{-1} . The difference between the observation and the DFT calculation may be caused by large anharmonicity of the wagging vibrational potential. We could not observe the other NH_2 wagging modes for the *trans*, 611 cm^{-1} , and *cis*, 604 cm^{-1} , isomers, probably because they are out of range of our spectral measurement. The weak bands appearing at 763 and 678 cm^{-1} may be assigned to the *trans* and *cis* isomers, respectively. Thus, we conclude that the *trans* and *cis* isomers of 1,4-diaminobenzene coexist in the matrix. The observed and calculated wavenumbers for 1,4-diaminobenzene are summarized in Table 1 with the relative intensities.

3.2. Identification of the Photoreaction Intermediate 4-Aminoanilino Radical.

When the matrix sample of 1,4-diaminobenzene was exposed to UV light shorter than 350 nm after the measurement of Figure 1, spectral changes due to photoreaction were observed. Figure 2a shows a difference spectrum between those measured before and after UV irradiation through a UV-34 filter ($\lambda > 330\text{ nm}$) for 10 min. The increasing and decreasing bands are ascribed to photoproducts and the reactant, respectively. The observed increasing bands are divided into two groups; intensities of the bands marked with “x” are unchanged during annealing up to 28 K, while those of the others decrease. This means that the former bands are assignable to a stable photoproduct, while the latter bands are assignable to a transient species which is unstable at matrix temperature higher than 28 K. Figure 2b shows a difference spectrum between those measured after and before the annealing,

TABLE 1: Observed and Calculated Wavenumbers (cm⁻¹) and Their Relative Intensities of 1,4-Diaminobenzene

obsd		calcd, <i>trans</i>			calcd, <i>cis</i>		
ν	int	ν^a	int	sym	ν^a	int	sym
3477	2.1	3586	0	b _g	3588	4.9	b ₁
3467	5.5	3586	3.8	a _u	3588	0	a ₂
3396	2.3	3486	0	a _g	3487	2.9	b ₂
3387	4.2	3485	2.5	b _u	3487	0.3	a ₁
3062	0.9	3122	0	a _g	3119	0.0	a ₁
3059	1.8	3119	6.9	a _u	3116	9.1	b ₁
3043	1.6	3104	0	b _g	3101	0	a ₂
3034	1.7	3103	6.8	b _u	3101	8.9	b ₂
3030	2.4						
3018	1.4						
1616	16.8	1649	0	a _g	1648	0.7	a ₁
		1630	23.5	b _u	1629	26.2	b ₂
		1625	0	a _g	1625	4.4	a ₁
		1602	0	b _g	1602	0	a ₂
1521	100	1523	38.3	b _u	1523	50.1	b ₂
		1458	0.0	a _u	1458	0.0	b ₁
1322	2.9	1335	3.8	a _u	1335	5.0	b ₁
1312	1.9	1331	0	b _g	1331	0	a ₂
		1273	0	a _g	1272	0.0	a ₁
1263	24.4	1258	23.1	b _u	1258	30.5	b ₂
		1179	0	a _g	1179	0.0	a ₁
1128	8.3	1135	2.7	a _u	1135	3.6	b ₁
1083 ^b	15.1						
1032 ^b	6.2	1096	0	b _g	1095	0	a ₂
1010	0.9	1047	0.3	a _u	1046	0.4	b ₁
		1002	0.0	b _u	1002	0.0	b ₂
		915	0.0	a _u	916	0	a ₂
		899	0	a _g	900	0.1	b ₂
		840	0	a _g	841	1.1	a ₁
822	17.0	811	16.8	b _u	810	19.8	a ₁
		789	0	b _g	790	0.0	b ₁
763 ^c	2.3	760	0.2	b _u	763	0.0	b ₂
678 ^d	3.5	699	0	a _g	687	3.8	b ₂
		646	0	b _g	646	0	a ₂
688 ^d	32.9	638	0	a _g	641	34.4	a ₁
e		611	100	b _u	604	100	b ₂

^a A scaling factor of 0.98 is used. ^b May be assigned to combination bands. See the text. ^c Assigned to the *trans* isomer. ^d Assigned to the *cis* isomer. ^e Out of the range of our spectral measurement.

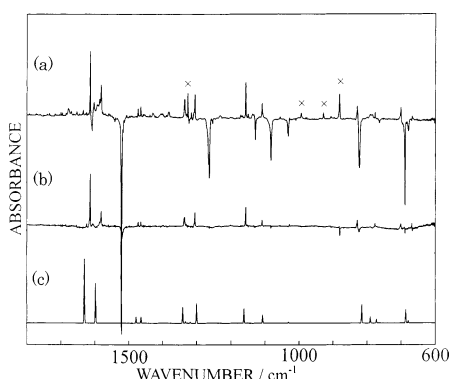


Figure 2. Difference spectra of 1,4-diaminobenzene: (a) between spectra measured before and after UV irradiation through a UV-32 filter for 10 min; (b) between spectra measured after and before annealing up to 28 K after the irradiation (bands marked with “x” are due to an unknown photoproduct); (c) calculated spectral pattern of 4-aminoanilino radical obtained by DFT/B3LYP/6-31++G** using a scaling factor of 0.98.

where the stable photoproduct bands disappear because their intensities are unchanged during the annealing. Since the calculated spectral pattern of 4-aminoanilino radical obtained by the DFT calculation shown in Figure 2c reproduces the observed spectrum shown in Figure 2b satisfactorily, we conclude that the UV photolysis of 1,4-diaminobenzene yields 4-aminoanilino radical by dissociation of one hydrogen atom of the amino groups. We assume that the photodetached

TABLE 2: Observed and Calculated Wavenumbers (cm⁻¹) and Their Relative Intensities of 4-Aminoanilino Radical

obsd		calcd		approximate assignment ^b
ν	int	ν^a	int	
3528	15.2	3634	13.2	$\nu(\text{NH}_2)$
3429 ^c	42.4	3520	32.6	$\nu(\text{NH}_2)$
		3366	2.7	$\nu(\text{N}-\text{H})$
		3148	1.6	$\nu(\text{C}-\text{H})$
		3122	6.4	$\nu(\text{C}-\text{H})$
		3109	8.2	$\nu(\text{C}-\text{H})$
		3102	7.6	$\nu(\text{C}-\text{H})$
1614	100	1631	100	NH ₂ scissoring
1582	30.9	1598	62.2	$\nu(\text{C}=\text{C})$, NH ₂ scissoring
		1527	0.4	$\nu(\text{C}=\text{C})$, NH ₂ rocking
1472	8.6	1478	9.7	$\nu(\text{C}=\text{C})$
1464	9.6	1463	9.8	$\nu(\text{C}=\text{C})$
1335	16.0	1340	25.1	$\nu(\text{C}=\text{N})$
1330	3.5	1332	2.7	$\nu(\text{C}-\text{C})$, $\beta(\text{N}-\text{H})$, NH ₂ rocking
		1318	1.9	$\beta(\text{C}-\text{H})$
1305	26.6	1300	30.5	$\nu(\text{C}-\text{N})$
1157	37.0	1162	22.4	$\beta(\text{C}-\text{H})$, $\beta(\text{N}-\text{H})$
1151	2.3	1152	0.8	$\beta(\text{C}-\text{H})$, $\beta(\text{N}-\text{H})$
1109	11.4	1107	12.7	$\beta(\text{C}-\text{H})$, NH ₂ rocking
1028	3.3	1031	1.8	NH ₂ rocking
977 ^c	1.2	975	0.4	$\beta(\text{C}-\text{H})$
		942	0.0	$\gamma(\text{C}-\text{H})$
		915	0.0	$\gamma(\text{C}-\text{H})$
		823	0.2	ring breathing
828	13.0	815	28.5	$\gamma(\text{C}-\text{H})$
791	0.4	790	9.7	$\gamma(\text{C}-\text{H})$, $\gamma(\text{N}-\text{H})$
776	6.3	772	6.0	ring breathing
701	10.1	686	20.6	$\gamma(\text{N}-\text{H})$
695	2.2	679	3.7	$\gamma(\text{C}-\text{C}-\text{C})$, $\gamma(\text{N}-\text{H})$
633	2.1	631	0.3	$\beta(\text{C}-\text{C}-\text{C})$

^a A scaling factor of 0.98 is used. ^b The symbols ν , β , and γ represent stretching, in-plane bending, and out-of-plane bending, respectively. ^c Splitting bands.

hydrogen atom recombines with aminoanilino radical to produce the original reactant 1,4-diaminobenzene at matrix temperature higher than 28 K. One may have a question as to whether the decreasing rate of the reactant bands is smaller than that expected. This may be explained by the assumption that a small amount of the reactant is pumped out during the annealing. The intense band appearing at 1614 cm⁻¹ is assignable to the NH₂ scissoring mode of aminoanilino radical, and the 1350 cm⁻¹ band to the C–N stretching mode. The observed and calculated wavenumbers are summarized in Table 2 with the relative intensities and approximate vibrational assignments.

Ernstbrunner et al. observed a resonance Raman spectrum of a radical cation in the photolysis of 1,4-diaminobenzene instead of 4-aminoanilino radical.¹¹ Since they photolyzed the sample in a protonic matrix at 77 K, they detected 1,4-diaminobenzene radical cation stabilized by interaction with the solutions, but not 4-aminoanilino radical. This cation is easily produced in solutions of 1,4-diaminobenzene halide known as Würster's salts^{18–20} and produced by 187 nm laser irradiation of a supersonic molecular beam.²¹ In contrast to this radical cation, no experimental evidence for 4-aminoanilino radical has been obtained till the present study.

To identify the unknown species marked with “x”, we compared the observed spectrum with calculated spectral patterns of 1,4-diaminobenzene radical cation and possible photoproducts such as aniline radical cation, Dewar-type 1,4-diaminobenzene, and so on. However, no calculated spectral patterns were consistent with the unknown species bands. Therefore, identification of the unknown species remains unresolved in this work.

3.3. Photoisomerization of the Final Products, *trans*- and *cis*-2,5-Cyclohexadiene-1,4-diimine. When the matrix sample

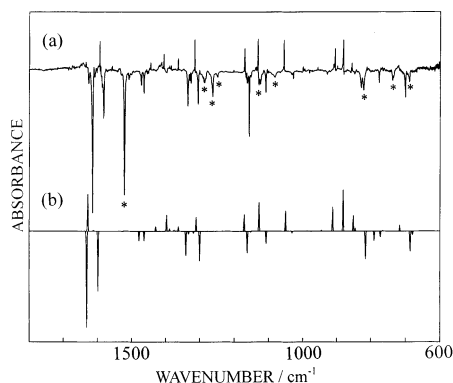
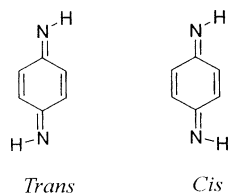


Figure 3. Difference spectrum between those measured before and after UV irradiation through a UV-28 filter for 20 min after the UV-32 irradiation for 120 min: (a) observed spectrum; (b) calculated spectral pattern obtained by DFT/B3LYP/6-31++G** using a scaling factor of 0.98. A mixture of *trans*- and *cis*-2,5-cyclohexadiene-1,4-diimine bands are shown upside, and 4-aminoanilino radical bands downside. The bands marked with an asterisk in the observed spectrum are due to 1,4-diaminobenzene remaining in the first photolysis.

SCHEME 4



was exposed to the shorter-wavelength UV light, the infrared spectra of the final products were observed. Figure 3a shows a difference spectrum between those measured before and after UV-28 irradiation ($\lambda > 270$ nm) for 20 min after the UV-32 irradiation ($\lambda > 310$ nm) for 120 min. The decreasing bands are due to 4-aminoanilino radical and the reactants remaining in the first photolysis, while the increasing bands are due to the final products. To identify the final products, we have performed DFT calculations of the most plausible candidate, i.e., 2,5-cyclohexadiene-1,4-diimine, which is produced from 4-aminoanilino radical by dissociation of one hydrogen atom of the other amino group.

This final product, 2,5-cyclohexadiene-1,4-diimine, is planar and has two conformations, *cis* and *trans*, around the C=N bonds, as shown in Scheme 4.

Although infrared and electronic absorption spectra of 2,5-cyclohexadiene-1,4-diimine in film or solution were previously measured,^{22–24} conformational analyses were not complete.²⁴ The calculated spectral patterns of a mixture of *trans*- and *cis*-2,5-cyclohexadiene-1,4-diimine obtained by the present study are compared with the obtained spectrum in Figure 3. Since the calculated pattern reproduces the observed difference spectrum satisfactorily, we conclude that the final photoproduct bands are assignable to a mixture of *trans*- and *cis*-2,5-cyclohexadiene-1,4-diimine.

The energy difference between the more stable isomer, *trans*, and the less stable isomer, *cis*, is calculated to be 1.45 kJ mol^{−1}, while the isomerization barrier is 116.7 kJ mol^{−1}. When the matrix sample was irradiated by the other wavelength UV light, spectral changes due to photoisomerization between the *trans* and *cis* isomers were observed. Figure 4a shows a difference spectrum between those measured before and after UV-34 irradiation ($\lambda > 330$ nm) for 10 min after the UV-32 irradiation (200 < λ < 400 nm) for 180 min; 2,5-cyclohexadiene-1,4-diimine is produced from 4-aminoanilino radical by the latter

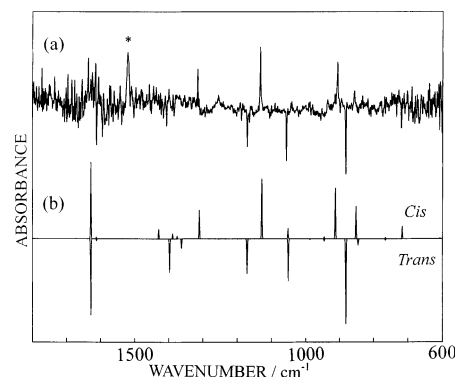


Figure 4. Difference spectrum between those measured before and after UV irradiation through a UV-34 filter for 10 min after measurement of Figure 3: (a) observed spectrum, where a broad band marked with an asterisk is due to the reactant 1,4-diaminobenzene appearing artificially; (b) calculated spectral patterns of 2,5-cyclohexadiene-1,4-diimine obtained by DFT/B3LYP/6-31++G** using a scaling factor of 0.98. *Trans* bands are shown downside and *cis* bands upside.

irradiation, and *trans*–*cis* photoisomerization is induced by the former irradiation. This spectral change is compared with the calculated spectral pattern shown in Figure 4b. The calculated pattern reproduces the observed pattern satisfactorily. The observed and calculated wavenumbers and relative intensities for *trans*- and *cis*-2,5-cyclohexadiene-1,4-diimine are summarized in Table 3. The bands appearing in the region between 1500 and 600 cm^{−1} are consistent with the corresponding calculated wavenumbers within 9 cm^{−1}, except for the *trans* band appearing at 1165 cm^{−1}, which may be assigned to a combination band or a splitting band due to Fermi resonance.

We have also found that the *trans* and *cis* isomers exist in a photoequilibrium state in the matrix during irradiation and that the *cis* population decreases as the irradiation wavelength shortens. For example, the absorbance ratio between the *cis* band at 1132 cm^{−1} and the *trans* band at 881 cm^{−1} is estimated to be 0.68 ± 0.03 upon UV-34 irradiation ($\lambda > 330$ nm), while the ratio decreases to 0.61 ± 0.03 upon UV-28 irradiation ($\lambda > 270$ nm). This finding implies that the electronic absorption of the *cis* isomer slightly shifts to the shorter-wavelength side from that of the *trans* isomer if the absorption coefficient of the *cis* isomer is nearly equal to that of the *trans* isomer. Measuring the absorption spectra for the *cis* and *trans* isomers separately seems to be useful for confirmation of this assumption; however, it has not been achieved.²³

3.4. Optimized Geometries of 1,4-Diaminobenzene, 4-Aminoanilino Radical, and 2,5-Cyclohexadiene-1,4-diimine. From the vibrational analyses of the observed infrared spectra with the aid of the DFT calculation, we conclude that the π -conjugated system of 1,4-diaminobenzene changes to a quinone type in 2,5-cyclohexadiene-1,4-diimine through a semiquinone type in 4-aminoanilino radical. This conclusion is confirmed by the calculations of the optimized geometries for 1,4-diaminobenzene, 4-aminoanilino radical, and 2,5-cyclohexadiene-1,4-diimine at the same DFT/B3LYP/6-31++G** level. The obtained bond lengths are compared with one another in Figure 5. The geometrical parameters of 1,4-diaminobenzene correspond to the experimental data obtained by electron diffraction¹² within an error of 0.8%, which is also consistent with previous calculations.^{12–14,25}

The imino group of 4-aminoanilino radical is in the benzene plane, while the amino group is bent out of the plane by 27.7°. This value is smaller than that of 1,4-diaminobenzene, 40.5°. The bond angle of H–N–H is 114.4° and 110.8° for 4-aminoanilino radical and 1,4-diaminobenzene, respectively. This

TABLE 3: Observed and Calculated Wavenumbers (cm⁻¹) and Their Relative Intensities of 2,5-Cyclohexadiene-1,4-diimine

<i>trans</i> isomer					<i>cis</i> isomer					obsd ^b ν	
obsd		calc		sym	obsd		calcd		sym		
ν	int	ν^a	int		ν	int	ν^a	int			
1594 ^c	63.1	3374	0	a _g	1594 ^c		3373	3.2	a ₁	3173	
		3374	6.5	b _u			3373	3.9	b ₂		
		3148	0	a _g			3156	2.3	a ₁		
		3147	4.6	b _u			3139	0.1	b ₂		
		3112	0	a _g			3121	8.7	a ₁		
		3112	7.4	b _u			3102	2.8	b ₂		
		1671	0	a _g			1672	0.1	a ₁		
		1628	89.4	b _u			1628	100	b ₂		1594
		1611	2.6	b _u			1612	2.3	a ₁		1585
1406	43.8	1575	0	a _g	1426	11.1	1575	0.1	a ₁	1433	
		1429	0	a _g			1429	12.6	b ₂		
		1397	39.2	b _u			1388	6.7	a ₁		
1364	18.8	1362	11.0	b _u	1374	33.3	1375	3.7	b ₂	1366	
		1315	0	a _g			1310	37.6	b ₂		
1170	56.3	1171	40.4	b _u	1315	88.9	1172	0.5	a ₁	1221	
1165 ^d	25.0	1166	0	a _g			1168	0.2	a ₁		
		1129	0	a _g	1132	100	1128	78.3	b ₂		
1056 ^c	84.4	1050	48.9	b _u	1056 ^c		1051	13.3	a ₁	1075/1072	
		987	1.0	a _u			990	0	a ₂		1010
		975	0	b _g			969	0	a ₂		962
		945	2.5	b _u			945	2.8	b ₂		936
881	100	912	0	b _g	906	77.8	912	66.0	b ₁	859/854	
		881	100	a _u			873	0	a ₂		
		845	7.5	a _u			851	42.1	b ₁		
		779	0	a _g	856	25.9	779	0.1	a ₁		
		765	1.7	b _u			765	2.0	b ₂		
		724	0	b _g			728	0	a ₂		
		704	0	b _g	722	11.1	716	16.3	b ₁		
		607	0	a _g			607	1.4	b ₂		

^a A scaling factor of 0.98 is used. ^b Measured in a solid film.²⁴ ^c *Trans* and *cis* bands are overlapped. ^d Assigned to a combination mode, overtone, or Fermi coupling.

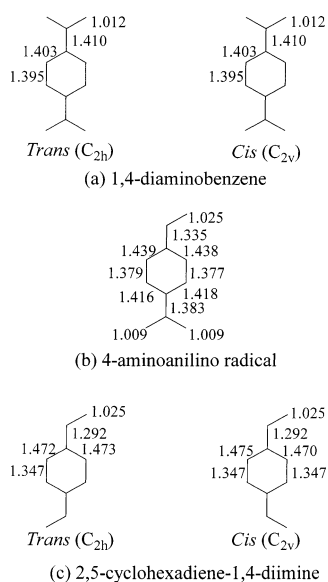
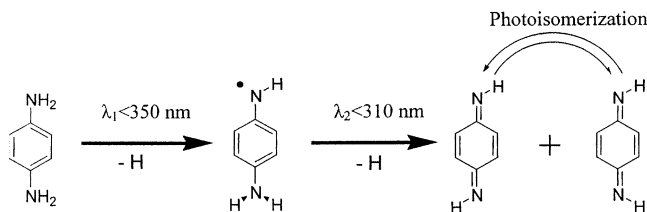


Figure 5. Optimized bond lengths of 1,4-diaminobenzene, 1,4-diaminobenzene radical cation, 4-aminoanilino radical, and 2,5-cyclohexadiene-1,4-diimine calculated at the DFT/B3LYP/6-31++G** level. The numbers represent C–C, C–N, and N–H bond lengths in angstroms.

finding implies that the amino group of 4-aminoanilino radical is in the middle between sp² (120°) and sp³ (109.5°). On the other hand, all the C–N and C–C bond lengths of 4-aminoanilino radical are between the corresponding bond lengths of 1,4-diaminobenzene and 2,5-cyclohexadiene-1,4-diimine. For example, the C–N bond lengths are calculated to be 1.410, 1.383/1.335, and 1.292 Å for 1,4-diaminobenzene, amino/imino side of the 4-aminoanilino radical, and 2,5-cyclohexadiene-1,4-diimine, respectively. The benzene ring of 4-aminoanilino

SCHEME 5



radical is slightly distorted, where the C=C lengths at the imino group side are about 0.02 Å longer than those at the amino group side. This distortion is also found in the structure of *p*-benzosemiquinone radical in the hydroquinone and 1,4-benzoquinone system.⁴

3.5. Photoreaction Mechanism of 1,4-Diaminobenzene. We summarize the photoreaction mechanism of 1,4-diaminobenzene in the low-temperature argon matrix as follows: (1) No reaction occurs when the irradiation wavelength is longer than 350 nm. (2) 4-Aminoanilino radical is produced from 1,4-diaminobenzene when the irradiation wavelength is shorter than 350 nm. (3) 2,5-Cyclohexadiene-1,4-diimine is produced from 4-aminoanilino radical when the irradiation wavelength is shorter than 310 nm. (4) Photoisomerization between *trans*- and *cis*-2,5-cyclohexadiene-1,4-diimine occurs, where the *trans* isomer changes to the *cis* isomer by longer-wavelength irradiation and the *cis* isomer changes to the *trans* isomer by shorter-wavelength irradiation. The photoreaction pathway from 1,4-diaminobenzene to 2,5-cyclohexadiene-1,4-diimine via 4-aminoanilino radical is shown in Scheme 5.

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