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Photoisomerization and photocyclization of 3,5-cyclohexadiene-1,2-diimine and its methyl-substituted derivatives in low-temperature argon matrices

Kenji Ujike, Nobuyuki Akai, Satoshi Kudoh, Munetaka Nakata*

Graduate School of BASE (Bio-Applications and Systems Engineering), Tokyo University of Agriculture and Technology, Naka-cho, Koganei, Tokyo 184-8588, Japan

Abstract

3,5-Cyclohexadiene-1,2-diimine was produced from 1,2-diaminobenzene in a low-temperature argon matrix by UV irradiation ($\lambda < 270$ nm). Conformational changes from *cis–cis* to *cis–trans* and *trans–trans* were induced upon irradiation of $\lambda > 410$ nm, while the shorter-wavelength irradiation of $410 > \lambda > 350$ nm resulted in photoisomerization from *cis–trans* to *cis–cis* in addition to photocyclization to yield 7,8-diazabicyclo[4.2.0]octa-1,3,5-triene. This photocyclization mainly occurred upon irradiation of $350 > \lambda > 290$ nm. Similar spectral changes due to photoisomerization among the four isomers of 4-methyl-3,5-cyclohexadiene-1,2-diimine and among the three of 4,5-dimethyl-3,5-cyclohexadiene-1,2-diimine were observed, but not due to photocyclization. The wavelength dependence for the photoisomerization and the methyl-substitution effect for the photocyclization were elucidated in terms of the π–π* and n–π* vertical transition energies and oscillator strengths obtained by the time-dependent density functional theory (DFT) calculation.
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Keywords: Matrix isolation; Infrared spectra; Density functional theory calculation; Photoisomerization; Photocyclization; 3,5-Cyclohexadiene-1,2-diimine; 7,8-Diazabicyclo[4.2.0]octa-1,3,5-triene

1. Introduction

Aromatic amines, which are produced by biological and chemical reductions of azo dies, are noticeable compounds in the environmental health chemistry [1]. For example, 1,2-diaminobenzene is suspected to be a carcinogenic compound, and its use in cosmetic industry is inhibited [2]. It is one of the urgent subjects to examine the chemical and physical reactions of diaminobenzenes. Recently, we investigated the photoreaction of 1,4-diaminobenzene in low-temperature rare-gas matrices and reported on the elimination of hydrogen atoms in the amino groups upon UV irradiation as shown in Scheme 1 [3].

Infrared bands of an intermediate produced from 1,4-diaminobenzene upon UV irradiation ($\lambda > 350$ nm) were assigned to 4-aminoanilino radical, while a final product produced from the 4-aminoanilino radical upon shorter-wavelength irradiation ($\lambda > 310$ nm) was identified as 2,5-cyclohexadiene-1,4-diimine. This π-conjugation conversion is similar to that of the well-known hydroquinone and 1,4-benzoquinone system (Scheme 2).

In contrast to *p*-benzoquinone, the *trans–cis* photoisomerization around the two C=N bonds of 2,5-cyclohexadiene-1,4-diimine was observed, where the *cis/trans* population ratio depends on the irradiation wavelength.

In the present study, we have investigated the photoreactions of 1,2-diaminobenzene, 4-methyl-1,2-diaminobenzene, and 4,5-dimethyl-1,2-diaminobenzene by the same method. In analogy with the photoreaction of 1,4-diaminobenzene, one of the final products of 1,2-diaminobenzene might be 3,5-cyclohexadiene-1,2-diimine, hereafter denoted as CHDI. This corresponds to *o*-benzoquinone, which is less stable than *p*-benzoquinone. One of

* Corresponding author. Tel./fax: +81 42 388 7349.
  E-mail address: necom@cc.tuat.ac.jp (M. Nakata).
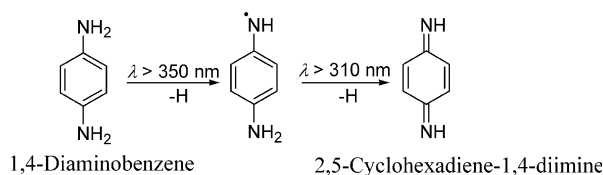
Scheme 1.
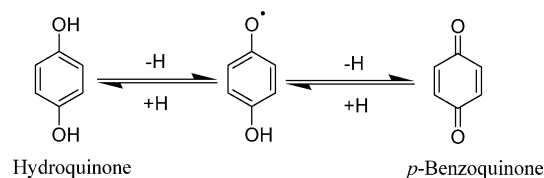
Scheme 2.

the purposes in the present study is to examine the photoisomerization among the three isomers of CHDI displayed in Fig. 1. First, we confirm the photoisomerization upon various wavelengths irradiation reported by two research groups [4,5], who produced CHDI in the photo-reaction of 2-aminophenyl azide by elimination of N_2 and migration of a hydrogen atom. Second, in addition to the photoisomerization, we report on the photocyclization to yield 7,8-diazabicyclo[4.2.0]octa-1,3,5-triene, hereafter denoted as DABO. Third, the results of photoreaction for

CHDI are compared with those for 4-methyl-CHDI and 4,5-dimethyl-CHDI produced from the corresponding methyl-substituted 1,2-diaminobenzenes. The wavelength dependence of the photoisomerization and the methyl-substitution effect for the photocyclization are elucidated in terms of the π–π^* and n–π^* vertical transition energies and oscillator strengths obtained by the time-dependent DFT calculation.

2. Experimental and calculations

1,2-Diaminobenzene (purity > 96%), 4-methyl-1,2-dia-minobenzene (purity > 98%) and 4,5-dimethyl-1,2-diami-nobenzene (purity > 95%), purchased from Tokyo Chemical Industry, were used after vacuum distillation. A small amount of 1,2-diaminobenzene was placed in a glass tube in the way of a deposition system [6], while solid samples of 4-methyl-1,2-diaminobenzene and 4,5-dimethyl-1,2-diamino-benzene were placed in a stainless steel pipe with a heating system and warmed to about 310 and 320 K, respectively, to obtain sufficient vapor pressure. UV light coming from a superhigh-pressure mercury lamp was used to induce photoreaction. A water filter was used to remove thermal reactions, and L42, UV36, UV30 and UV28 short-wavelength cutoff filters were used to select irradiation wavelength. Other experimental details were reported elsewhere [6,7].
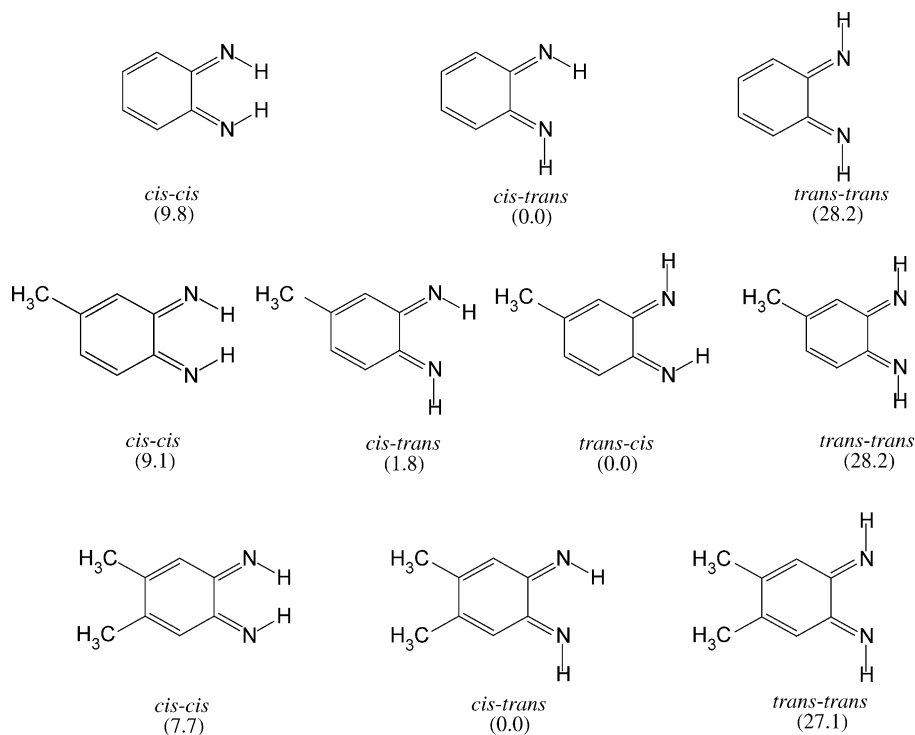

Fig. 1. Possible isomers for 3,5-cyclohexadiene-1,2-diimine, 4-methyl-3,5-cyclohexadiene-1,2-diimine and 4,5-dimethyl-3,5-cyclohexadiene-1,2-diimine. The numbers in parentheses represent relative energies in units of kJ mol^{-1} obtained by DFT/B3LYP/6-31+ +G** calculation.
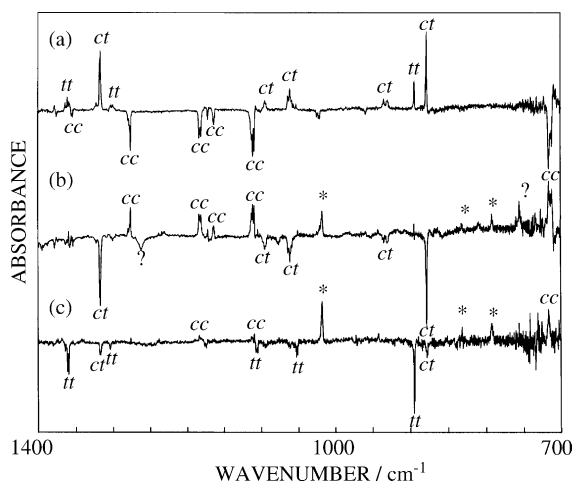
Fig. 2. Spectral changes due to photoisomerization of 3,5-cyclohexadiene-1,2-diimine. (a) L42 ($\lambda > 410$ nm) irradiation for 90 min, (b) UV36 ($\lambda > 350$ nm) irradiation for 90 min, (c) UV30 ($\lambda > 290$ nm) irradiation for 20 min, expanded two times. Bands marked with * are due to *trans*-7,8-diazabicyclo[4.2.0]octa-1,3,5-triene. Bands marked with question marks remain unassigned; they may be impurities.

DFT calculations were performed using the GAUSSIAN 03 program [8] 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 and to obtain infrared spectral patterns. The time-dependent DFT (TD-DFT) calculation [11] was performed to estimate vertical transition energies and oscillator strengths from S_0 to S_1 and S_2 states.

3. Results and discussion

3.1. Photoreaction of 1,2-diaminobenzene

In a recent letter [6], we have reported on the result of photolysis of 1,2-diaminobenzene, where the three isomers around the two C=N bonds, *cis–trans* (*ct*), *cis–cis* (*cc*) and *trans–trans* (*tt*), of CHDI shown in Fig. 1 are found to be produced by UV irradiation. Their vibrational assignments, including the observed and calculated wavenumbers with the relative intensities, are reported in the letter. Photocyclization of CHDI to produce a bicyclo form, DABO, is also described there. Here, we focus our interest on the wavelength dependences of conformational changes among the three isomers of CHDI and its photocyclization to produce DABO.
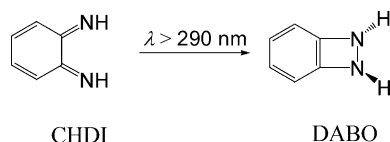
Scheme 3.

Table 1
Dependence of photoisomerization and photocyclization on irradiation wavelength (in nm)[a]

Molecules	$\lambda > 410$	$410 > \lambda > 350$	$350 > \lambda > 290$
CHDI	$cc \rightarrow ct$	$ct \rightarrow cc$	$tt \rightarrow cc$
	$cc \rightarrow tt$	$ct \rightarrow \text{DABO}$	$tt \rightarrow \text{DABO}$
4-Methyl-CHDI	$cc \rightarrow ct$ and tc	ct and $tc \rightarrow cc$	$tt \rightarrow cc$
		ct and $tc \rightarrow tt$	
4,5-Dimethyl-CHDI	$cc \rightarrow ct$	$ct \rightarrow cc$	$tt \rightarrow cc$
	$cc \rightarrow tt$		

[a] CHDI and DABO represent 3,5-cyclohexadiene-1,2-diimine and 7,8-diazabicyclo[4.2.0]octa-1,3,5-triene, respectively.

Subsequently to the irradiation without optical filters to produce CHDI from 1,2-diaminobenzene, the matrix sample was exposed to UV light through an L42 optical filter ($\lambda > 410$ nm) for 90 min, resulting in that the spectral changes due to photoisomerization were observed, as shown in Fig. 2a. It is found that the *cc* bands decreased and the *ct* and *tt* bands increased. On the other hand, the shorter-wavelength irradiation through a UV36 optical filter ($\lambda > 350$ nm), different spectral changes due to photoisomerization were observed. Fig. 2b shows a difference spectrum between the spectra measured after 90-min UV36 irradiation and 90-min L42 irradiation. The *ct* bands decreased and the *cc* bands increased, while the *tt* bands remained unchanged. In addition to the spectral changes due to the photoisomerization, new bands marked with * appeared. By a comparison with the calculated spectral patterns of possible candidates for photoproducts, they were identified as *trans*-DABO produced from CHDI by (Scheme 3) photocyclization [6].

The vibrational assignments, the observed and calculated wavenumbers, and their relative intensities for *trans*-DABO

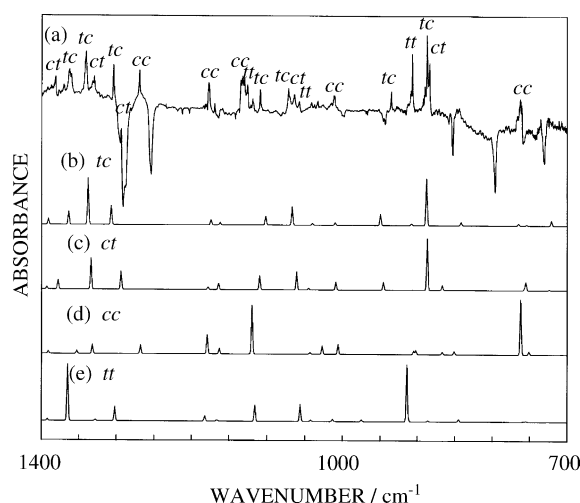Fig. 3. Infrared spectra of products in photolysis of 4-methyl-1,2-diaminobenzene. (a) Difference between spectra measured before and after UV irradiation without optical filters for 60 min, spectra (b)–(e) are calculated patterns of *trans–cis* (*tc*), *cis–trans* (*ct*), *cis–cis* (*cc*), and *trans–trans* (*tt*) 4-methyl-3,5-cyclohexadiene-1,2-diimine obtained by DFT/B3LYP/6-31++G** using a scaling factor of 0.98.

Table 2
Observed and calculated wavenumbers (in cm^{-1}) and their relative intensities of 4-methyl-3,5-cyclohexadiene-1,2-diimine

Trans–cis				Cis–trans				Cis–cis				Trans–trans			
Observed		Calculated		Observed		Calculated		Observed		Calculated		Observed		Calculated	
ν	Intensities	ν^a	Intensities	ν	Intensities	ν^a	Intensities		Intensities	ν^a	Intensities	ν	Intensities	ν^a	Intensities
		1391	13			1393	5			1391	5			1392	4
1360	27	1364	28	1381	22	1378	18			1353	6	1363	35	1365	100
1340	63	1338	99	1329	19	1334	60			1332	17			1328	2
1304	50	1307	40	1293	17	1294	35	1269	41	1268	16			1302	25
1169	9	1174	11			1178	5	1177	37	1179	34			1182	9
1159	7	1162	5			1164	12	1161	7	1163	10			1166	2
1109	25	1102	18	1119	9	1110	27	1130^b	100	1120	88	1126	38	1116	28
1072	28	1067	39	1064	22	1061	35	1040	5	1043	3	1057	11	1056	30
		1040	4			1045	3	1033	7	1027	15			1042	3
		1010	6			1009	16	1011^b	22	1006	18			1013	4
		987	<1			977	0			985	0			975	3
935	23	950	24			946	16			905	7	906	74	914	100
		908	4			906	<1			902	8			912	3
887	100	888	100	884	66	887	100			867	5			886	2
		842	8			867	9			851	6			845	5
		765	4			757	4	762	45	762	100			758	<1
		754	2			755	16			751	6			755	1
735	15	721	11			724	1			707	<1			726	<1

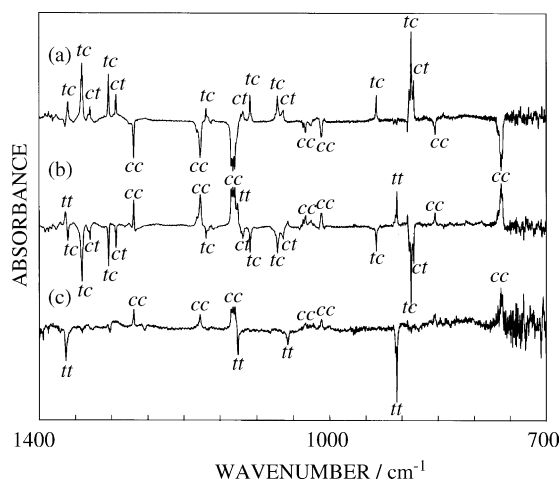[a] A scaling factor of 0.98 is used.
[b] The band exhibits splitting.

Fig. 4. Spectral changes due to photoisomerization of 4-methyl-3,5-cyclohexadiene-1,2-diimine. (a) L42 ($\lambda > 410$ nm) irradiation for 75 min, (b) UV36 ($\lambda > 350$ nm) irradiation for 35 min, (c) UV30 ($\lambda > 290$ nm) irradiation for 21 min, expanded three times.

were published elsewhere [6]. Subsequently to the UV36 irradiation, we exposed the matrix sample to UV light through a UV30 ($\lambda > 290$ nm) optical filter for 20 min. The difference spectrum is shown in Fig. 2c, where the *tt* bands decreased and the *trans*-DABO bands increased. The photocyclization from *tt* to *trans*-DABO mainly occurs, while the spectral change due to photoisomerization from *ct* to *cc* is small. The dependence of the photoisomerization and the photocyclization for CHDI on the irradiation wavelength is summarized in Table 1. Our observation on the photoisomerization is essentially consistent with the previous results on CHDI photo-produced from 2-aminophenyl azide [4,5].

3.2. Photoreaction of 4-methyl-1,2-diaminobenzene

3.2.1. Infrared spectra of 4-methyl-CHDI

The photoreaction of 4-methyl-1,2-diaminobenzene has been investigated by the same method as used in that of 1,2-diaminobenzene. Fig. 3a shows a difference spectrum between the spectra measured before and after 60-min UV irradiation without optical filters, where the photoproducts bands and the reactant bands increased and decreased, respectively. In analogy with the results of 1,4-diaminobenzene and 1,2-diaminobenzene, it is reasonable to assign the photoproduct bands to 4-methyl-CHDI. Geometrical optimization was performed, leading to the result that the four isomers of 4-methyl-CHDI shown in Fig. 1 are all stable. In contrast to CHDI, *tc* of 4-methyl-CHDI is non-equivalent to *ct*, where the latter is less stable than the former by 1.8 kJ mol^{-1}. The *cc* and *tt* isomers are less stable than *tc* by 9.1 and 28.2 kJ mol^{-1}, respectively. The calculated spectral patterns of the four isomers are compared with the observed spectrum in Fig. 3. The spectral pattern of *tc* is very similar to that of *ct*, however, the strongest bands around 890 cm^{-1} are distinguishable

from each other, i.e. the 888 and 887 cm^{-1} bands are assignable to the C–H and N–H out-of-plane bending mode of *tc* and *ct*, respectively. On the other hand, the intense bands at 906 and 762 cm^{-1} are assignable to the corresponding mode of the less stable isomers, *tt* and *cc*, respectively. All the other observed bands are consistent with the calculated values of the four isomers within 15 cm^{-1}. The observed and calculated wavenumbers with the relative intensities are summarized in Table 2.

3.2.2. Selective photoisomerization

Similar experiments on the selective-wavelength irradiation were performed using various optical filters. Fig. 4a shows a difference spectrum between the spectrum measured after L42 irradiation for 75 min and Fig. 3a. It is found that the *cc* bands decreased, while the *ct* and *tc* bands increased. When the matrix sample was exposed to UV light through a UV36 optical filter for 35 min after the L42 irradiation, the *tc* and *ct* bands decreased and the *cc* and *tt* bands increased, as shown in Fig. 4b. On the other hand, the UV30 irradiation showed that the *tt* bands decreased and the *cc* bands increased (Fig. 4c). The photoisomerization pathways for 4-methyl-CHDI are summarized in Table 1. No infrared bands of 4-methyl-DABO were observed despite the use of various optical filters.

3.3. Photoreaction of 4,5-dimethyl-1,2-diaminobenzene

3.3.1. Infrared spectra of 4,5-dimethyl-CHDI

Similar experiments for 4,5-dimethyl-1,2-diaminobenzene were performed by the same method. A difference spectrum between the spectra measured before and after 60-min UV irradiation without optical filters is shown in Fig. 5a, where the reactant and the photoproducts bands

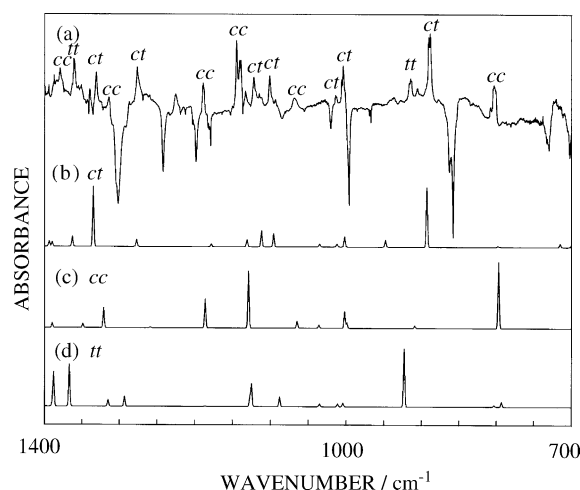Fig. 5. Infrared spectra of products in photolysis of 4,5-dimethyl-1,2-diaminobenzene. (a) Difference between spectra measured before and after UV irradiation without optical filters for 60 min, spectra (b)–(d) are calculated patterns of *cis–trans* (*ct*), *cis–cis* (*cc*), and *trans–trans* (*tt*) 4,5-dimethyl-3,5-cyclohexadiene-1,2-diimine, respectively, obtained by DFT/B3LYP/6-31 + +G** using a scaling factor of 0.98.

Table 3
Observed and calculated wavenumbers (in cm^{-1}) and their relative intensities of 4,5-dimethyl-3,5-cyclohexadiene-1,2-diimine

Cis–trans				Cis–cis				Trans–trans			
Observed		Calculated		Observed		Calculated		Observed		Calculated	
ν	Intensities	ν^a	Intensities	ν	Intensities	ν^a	Intensities	ν	Intensities	ν^a	Intensities
		1453	17	1440	96	1452	18			1454	17
		1448	0			1449	0			1448	0
		1407	27			1404	8	1405	31	1404	37
		1394	9	1379	28	1390	8			1390	5
		1390	8			1389	<1			1388	59
		1363	17	1351	7	1349	7	1360	43	1367	72
1331	51	1335	100	1313	15	1321	33			1315	11
1276	46	1277	12	1259	6	1259	2			1293	17
		1178	5	1189	44	1186	48			1186	<1
		1131	12			1130	1			1127	16
1123	35	1112	27	1145^b	100	1129	93	1133	21	1125	38
1101	39	1096	22	1068	12	1065	11			1088	16
		1045	<1			1043	0			1045	0
		1035	5			1036	5			1035	5
1014	12	1012	5	1006	30	1002	28			1011	5
1004	53	1002	17			999	9			1004	6
937	5	948	12			909	4	914	27	923	100
889	93	893	99			875	0			890	0
		870	<1			851	0			852	0
		798	2	802	48	797	100			803	3
		795	<1			797	10			793	9
		715	6			688	0			720	0

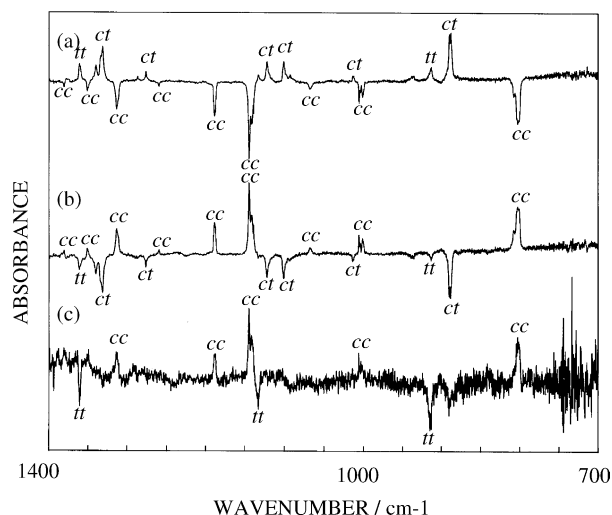^{a} A scaling factor of 0.98 is used.
^{b} The band exhibits splitting.

Fig. 6. Spectral changes due to photoisomerization of 4,5-dimethyl-3,5-cyclohexadiene-1,2-diimine. (a) L42 ($\lambda > 410$ nm) irradiation for 30 min, (b) UV36 ($\lambda > 350$ nm) irradiation for 30 min, (c) UV30 ($\lambda > 290$ nm) irradiation for 5 min, expanded nine times.

Table 4
Vertical transition energies (in nm) and oscillator strengths of CHDI, 4-methyl-CHDI, and 4,5-dimethyl-CHDI obtained by time-dependent DFT calculation

CHDI	Cis–cis	Cis–trans[a]		Trans–trans
π–π*	402.2	387.7		375.1
	(0.0667)[b]	(0.0815)		(0.0670)
n–π*	383.0	378.1		376.6
	(0.0026)	(0.0003)		(0.0003)
4-Methyl-CHDI	Cis–cis	Cis–trans	Trans–cis	Trans–trans
π–π*	404.5	386.2	393.1	375.6
	(0.0585)	(0.0712)	(0.0694)	(0.0827)
n–π*	376.9	368.9	374.9	372.1
	(0.0017)	(0.0003)	(0.0004)	(0.0002)
4,5-Dimethyl-CHDI	Cis–cis	Cis–trans[a]		Trans–trans
π–π*	412.1	396.2		381.4
	(0.0505)	(0.0620)		(0.0733)
n–π*	374.5	369.3		368.8
	(0.0017)	(0.0003)		(0.0000)

[a] *Trans–cis* is equivalent to *cis–trans*.
[b] Numbers in parentheses represent oscillator strengths.

decreased and increased, respectively. The calculated spectral patterns of the three isomers of 4,5-dimethyl-CHDI shown in Fig. 1 are compared with the observed spectrum. The *cc* and *tt* isomers are less stable than the most stable one, *ct*, by 7.7 and 27.1 kJ mol^{-1} like CHDI. All the observed bands are assignable to the three isomers, *ct*, *cc*, and *tt*, as shown in Fig. 5. The observed and calculated wavenumbers with the relative intensities are summarized in Table 3. They are consistent with each other within 16 cm^{-1}. It is concluded that the three isomers of 4,5-dimethyl-CHDI are produced in the photoreaction of 4,5-dimethyl-1,2-diaminobenzene.

3.3.2. Selective photoisomerization

After measuring Fig. 5a, the matrix sample was exposed to the UV light through an L42 optical filter for 30 min. The difference spectrum was shown in Fig. 6a, where the *cc* bands decreased and the *ct* and *tt* bands increased. Fig. 6b shows a spectral change due to the UV36 irradiation for 30 min subsequently to the L42 irradiation, where the *ct* bands decreased and the *cc* bands increased. On the other hand, the 5-min UV30 irradiation showed a spectral change (Fig. 6c), where the *tt* bands decreased and the *cc* bands increased. The photoisomerization pathways for 4,5-dimethyl-CHDI are compared with those of CHDI and 4-methyl-CHDI in Table 1. Infrared bands of 4,5-dimethyl-DABO produced from 4,5-dimethyl-CHDI by photocyclization were undetectable like 4-methyl-DABO.

3.4. Photoisomerization and vertical transition energies

As summarized in Table 1, the photo isomerization from *cc* to the other isomers mainly occurs upon L42 irradiation for CHDI, 4-methyl-CHDI, and 4,5-dimethyl-CHDI. On the other hand, the photoisomerization from *ct* and *tc* to other

isomers mainly occurs upon UV36 irradiation, while that from *tt* to others occurs upon UV30 irradiation. These findings suggest that *cc* absorbs longer-wavelength photons than *ct* and *tc*, which absorb longer-wavelength photons than *tt*. To confirm this assumption, we have estimated the vertical transition energies and the oscillator strengths from S_0 to S_1 and S_2 (π–π* and n–π*) using the time-dependent DFT method. The obtained values are shown in Table 4, where the S_1 and S_2 states are due to π–π* and n–π* transitions, respectively, except for *tt* of CHDI. It is found that the order of the vertical transition energies is *cc* < (*ct* and *tc*) < *tt* for the three compounds. This result is consistent with the observation summarized in Table 1, where *cc*, (*ct* and *tc*) and *tt* change to other isomers upon L42, UV36, and UV30 irradiation, respectively. A comparison between Tables 1 and 4 implies that the photoisomerization among the isomers occurs by excitation to the π–π* transition, which has large oscillator strengths.

3.5. Photocyclization and vertical transition energies

An infrared spectrum of *trans*-DABO is observable in the photoreaction of 1,2-diaminobenzene, but not *cis*-DABO. Since the infrared bands of *ct* decreased upon UV36 irradiation (Fig. 2b), *trans*-DABO seems to be produced from *ct*. This finding is consistent with the Woodward–Hoffman rule, which predicts that photocyclization of π-conjugated systems is disrotatory, resulting in that *ct* of CHDI yields *trans*-DABO, whereas *cc* and *tt* yield *cis*-DABO. On the other hand, the infrared bands of *tt* decreased upon UV30 irradiation (Fig. 2c) with an increase in the *trans*-DABO bands. To explain this fact, we propose

the following three reaction processes: (1) *Photoisomerization from tt to ct*: Photocyclization to yield *trans*-DABO occurs after the photoisomerization from *tt* to *ct* upon UV30 irradiation. This means that *ct* is an intermediate between *tt* and *trans*-DABO. (2) *Tunneling isomerization*: As reported in our recent paper [6], the relative energy of *cis*-DABO is higher than *trans*-DABO by 22 kJ mol^{-1}. If the hydrogen-atom inversion occurs by tunneling in relaxation from an electronically excited state, *cis*-DABO produced from *tt* may change to *trans*-DABO. Hydrogen-atom tunneling reactions in low-temperature matrices are known in other molecules such as hydroquinone [12], tetrachlorohydroquinone [13], and 1,2-dimethylhydrazine [14]. (3) *Transition from π–π* to n–π* state*: the photocyclization may occur on the potential surface of the n–π* state, where the repulsion between the two lone pairs of nitrogen atoms in the imino groups is weekend and the nitrogen atoms can approach each other to make a bond. If the Woodward–Hoffman rule is inapplicable to the n–π* state, then *tt* of CHDI can yield *trans*-DABO directly. This is plausible because the relative energy of n–π* of *tt* is below the π–π* state, as shown in Table 4. Then we can consider that the photocyclization to produce methyl-DABO and dimethyl-DABO is difficult because the relative energies of the n–π* states for all the isomers of methyl-CHDI and dimethyl-CHDI are higher than the π–π* states. This is consistent with the fact that no infrared bands of methyl-substituted DABO were observable in our spectra. However, further information is required to determine which process is a feasible one.

4. Conclusion remarks

The three torsional isomers of CHDI, *cis–cis*, *cis–trans*, and *trans–trans* around the two C=N bonds, are produced from 1,2-diaminobenzene upon UV irradiation ($\lambda < 270$ nm). The photoisomerization from *cc* to others occurs upon UV irradiation ($\lambda > 410$ nm), while that from *ct* to others upon $\lambda > 350$ nm and that from *tt* to others upon $\lambda > 290$ nm. Similar photoisomerization among the four isomers of 4-methyl-CHDI and among the three

isomers of 4,5-dimethyl-CHDI occurs. These wavelength-dependent photoisomerization is understandable in terms of the vertical transition energies to the π–π* state obtained by the time-dependent DFT calculation. On the other hand, *trans*-DABO is produced from CHDI by photocyclization, but not the case of methyl-substituted derivatives. This fact is understandable in terms of the vertical transition energies to the n–π* state. Since the n–π* state for *tt* of CHDI is below the π–π* state, *trans*-DABO can be produced after transition from the π–π* state to the n–π* state. As for methyl-substituted CHDI, the vertical transition energies for the n–π* states for all the isomers are higher than the π–π* states. Then methyl-substituted DABO cannot be produced from the corresponding CHDI.

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