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UV-induced single and double hydrogen-atom migrations in 3,6-diimino-1,4-cyclohexadiene-1,4-diamine in a low-temperature argon matrix

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Abstract

Isomerization induced by ultraviolet radiation due to intramolecular hydrogen-atom migration in 3,6-diimino-1,4-cyclohexadiene-1,4-diamine (DCD) was studied by matrix-isolation Fourier transform infrared (IR) spectroscopy and density functional theory (DFT) calculation. Two isomers produced by single and double inversion of the hydrogen atom(s) around the C=N bond(s) were identified using the wavelength dependence of the IR band-intensity changes. In addition, the IR bands of an intermediate produced by single hydrogen-atom transfer from the amino to the imino group ($C–NH_2\cdots NH=C$) in the hydrogen bond were measured and identified by a comparison with the calculated spectral patterns. These observations confirm stepwise photoisomerization of DCD.

1. Introduction

3,6-Diimino-1,4-cyclohexadiene-1,4-diamine (DCD, Fig. 1) has two intramolecular hydrogen bonds between the amino and imino groups ($C–HNH\cdots NH=C$). A problem of theoretical and experimental interest lies in whether or not single or double, proton or hydrogen-atom transfer occurs in this molecule. Single proton transfer was suggested by quantum-chemical calculations [1,2], where the structure of a zwitterion intermediate caused by single proton transfer was optimized using the AM1 and HF/3-21G and MP2/3-21G levels. Similar proton transfer in a phenyl-substituted derivative of DCD, azophenine, was studied by Rumpel et al. [3–5] who analyzed its isotopic NMR and IR spectra and suggested stepwise single hydrogen-atom transfer. However, no spectroscopic information on the intermediates caused by proton and hydrogen-atom transfer in DCD has yet been reported, to our knowledge.

We have recently investigated the photoisomerization of 3,5-cyclohexadiene-1,2-diimine and 2,5-cyclohexadiene-1,4-diimine produced from 1,2- and 1,4-diaminobenzenes, respectively, by UV irradiation by a joint analysis of low-temperature matrix-isolation IR spectroscopy and DFT calculation [6–8]. For 3,5-cyclohexadiene-1,2-diimine, which has an intramolecular hydrogen bond between the two imino groups ($C=NH\cdots NH=C$), UV-induced hydrogen-atom inversion around the C=N bonds was observed in the IR spectral changes upon irradiation with various wavelengths (Scheme 1). This finding implies that two kinds of hydrogen-atom migration are feasible in DCD, which has two intramolecular hydrogen bonds between the amino and imino groups: hydrogen-atom inversion around the C=N bonds and hydrogen-atom transfer within the hydrogen bond, as shown in Fig. 1. In the present Letter, we have isolated DCD in a low-temperature argon matrix and measured the IR spectra of the

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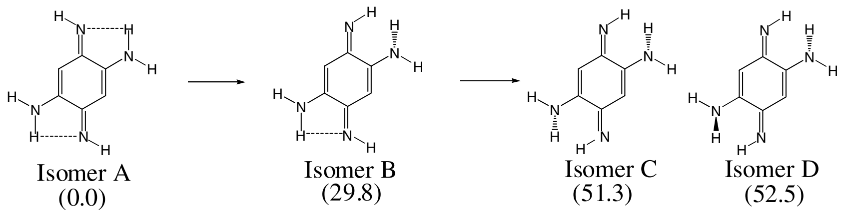
(a) Hydrogen-atom inversion



(b) Hydrogen-atom transfer

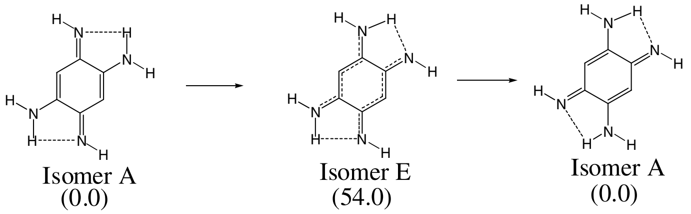
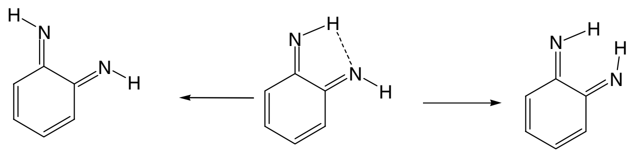


Fig. 1. Hydrogen-atom migration in 3,6-diimino-1,4-cyclohexadiene-1,4-diamine. Numbers in parentheses represent relative energies in kJ mol^{-1} obtained at the DFT/B3LYP/6-31++G** level. Isomers A and E are planar, while Isomers B, C, and D are non-planar with respect to one H atom of non-hydrogen-bonded amino groups. Isomer A is obtained by double H-atom transfer from the original Isomer A.



Scheme 1.

intermediates produced by single and double hydrogen migrations upon UV irradiation. The intermediates have been identified by a comparison of the observed spectra with the calculated IR spectral patterns to gain information on the mechanism of hydrogen migrations in DCD.

2. Experimental and calculation methods

A method to synthesize DCD was established by Nietzki and Hagenbach [9]. We prepared DCD as follows: A solid sample of 1,2,4,5-tetraaminobenznene tetrahydrochloride of 30 mg (purity > 93%, Aldrich) was solved in 15 ml distilled water. A solid sodium hydroxide (purity > 96%, Wako) of 17 mg was added to the solution. After evaporation of the solvent to dryness under reduced pressure, the residue was placed in a stainless steel pipe with a heating system and warmed to ≈463 K under 10^{-5} Pa to obtain sufficient vapor pressure. The vapor DCD was mixed with argon gas (purity 99.9999%, Nippon Sanso) and deposited in a vacuum chamber on a CsI plate, cooled by closed-cycle helium refrigeration (CTI Cryogenics, Model M-22) at ≈15 K. The matrix sample was exposed to UV light from a superhigh-pressure mercury lamp. A water filter was used to avoid thermal reactions, and UV30 and UV32 short-wavelength cutoff filters were used to select irradiation wavelength. Other experimental details were reported elsewhere [10–12].

DFT calculations were performed using the GAUSSIAN 03 program [13] with the 6-31++G** basis set. Becke's three-parameter hybrid density functional [14], in combination with the Lee–Yang–Parr correlation functional (B3LYP) [15], was used to optimize the geometrical structures and to obtain IR spectral patterns.

3. Results and discussion

3.1. Optimized structures

The geometrical structures of four stable isomers of DCD shown in Fig. 1 were optimized. Isomer A, which has two intramolecular hydrogen bonds between the amino and imino groups, is planar. On the other hand, Isomer B with one hydrogen bond is non-planar, where one hydrogen atom of the non-hydrogen-bonded amino group is ≈34° out of the benzene ring. Isomers C (asymmetric) and D (symmetric) are also non-planar, and one hydrogen atom of each amino group is ≈40° out of the ring. Their relative energies are 0, 29.8, 51.8, and 52.5 kJ mol^{-1} for Isomers A, B, C, and D, respectively, which reflect the number of intramolecular hydrogen bonds. The barrier height from Isomer C to D was estimated to be only 3.8 kJ mol^{-1}; this implies that Isomer D can isomerize to C under our experimental conditions. Hence, Isomer D was disregarded in the present analysis of the IR spectra.

We also performed the DFT/B3LYP/6-31++G** calculation for an intermediate, Isomer E, which is expected to be produced by single hydrogen-atom transfer from the amino to the imino group in Isomer A. The relative energy of Isomer E in the singlet state is 54.0 kJ mol^{-1} higher than Isomer A, being similar to that of Isomers C and D. The relative energy of Isomer E in the triplet state, also calculated using the same basis set, was found to be higher than that in the singlet state by ≈49 kJ mol^{-1}. Thus, only the singlet states were considered in the present analysis.

All the geometrical parameters for Isomer E were optimized, resulting in that this isomer is planar within 1°. Then we re-optimized the structure of Isomer E with assumption of planarity. The calculated bond lengths are listed in Table 1, where the numbering of atoms is given in Fig. 2a. The lengths of the C1—C6 and C3—C4 bonds, 1.512 Å, suggest single-bond character, while those of C1—C2 and C2—C3, 1.411 Å, and C4—C5 and C5—C6, 1.394 Å, are shorter than the single C—C bonds by ≈0.1 Å. Similarly, the C1—N3 and C3—N4 bonds, 1.314 Å, and C4—N1 and C6—N2, 1.329 Å, are shorter than the C—N single bonds. These comparisons suggest that the π-conjugation system in Isomer E is separated to the two parts; diimino part (N3—C1—C2—C3—N4) and diamino part (N2—C6—C5—C4—N1). The charge distribution on each atom is shown in Fig. 2b. The sum of the charge in the diimino part is about −0.55*e*, while that in the diamino part is +0.55*e*. This result implies that Isomer E is ≈55% ionic, where the imino and amino parts are charged negatively and positively, respectively. This means that a charge redistribution in the intermediate seems to occur with transfer of either a proton or a hydrogen atom.

Table 1
Calculated bond lengths (in Å) in Isomer E of DCD obtained at the DFT/B3LYP/6-31++G** level[a,b]

C1—C2	1.411	N1—H3	1.022
C2—C3	1.411	N1—H4	1.008
C3—C4	1.512	N2—H5	1.008
C4—C5	1.394	N2—H6	1.022
C5—C6	1.394	N3—H7	1.020
C1—C6	1.512	N4—H8	1.020
C1—N3	1.314	C2—H1	1.087
C3—N4	1.314	C5—H2	1.087
C4—N1	1.329		
C6—N2	1.329		

[a] Numbering of atoms is given in Fig. 2a.

[b] Other geometrical parameters are listed in Supplementary Material. They are also available upon request.

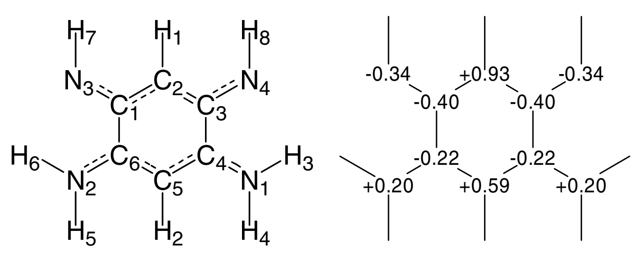


Fig. 2. Numbering of atoms in Isomer E (a) and charge distribution on each atom calculated at the DFT/B3LYP/6-31++G** level (b). The π-conjugation system is separated into two parts: diimine (N3—C1—C2—C3—N4) and diamine (N2—C6—C5—C4—N1).

3.2. Hydrogen-atom migration by UV irradiation

Seven intense bands were observed in the range of 700 and 1700 cm^{-1} in the IR spectrum of DCD measured before UV irradiation. This spectrum is compared in Fig. 3 with the spectral patterns for Isomers A, B, C and E calculated by the DFT method. The pattern for Isomer A, which is the most stable isomer with two intramolecular hydrogen bondings, reproduces the observed spectrum; the observed wavenumbers are consistent with the calculated values scaled by a factor of 0.98 within 17 cm^{-1}, as listed in Table 2.

When the matrix sample was exposed to UV light for 2 min through a UV 32 short-cut filter ($\lambda > 310$ nm), a spectral change was observed, as shown in the difference spectrum displayed in Fig. 4a. By a comparison between the observed and calculated patterns for the five isomers of DCD, the increasing bands were mainly assigned to Isomer B (Fig. 4b), while the decreasing bands were assigned to Isomer A. After this measurement, the sample was further exposed to UV light through a UV30 short-cut filter ($\lambda > 290$ nm) for 2 min. As shown in Fig. 4c, the intensities of the bands appearing at 1409, 1047

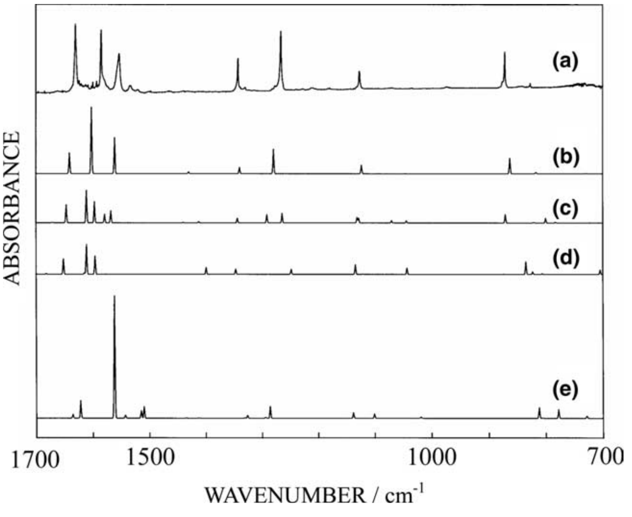


Fig. 3. Observed and calculated IR spectra of DCD: (a) observed after deposition; (b)–(e) calculated spectral patterns of Isomers, A, B, C, and E, respectively, obtained at the DFT/B3LYP/6-31++G** using a scaling factor of 0.98.

Table 2
Observed and calculated wavenumbers (in cm^{-1}) and their relative intensities of four isomers of DCD

Isomer A				Isomer B				Isomer C				Isomer E			
Obs.		Calc.		Obs.		Calc.		Obs.		Calc.		Obs.		Calc.	
v	Int.[a]	v^b	Int.[a]	v	Int.[a]	v^b	Int.[a]	v	Int.[a]	v^b	Int.[a]	v	Int.[a]	v^b	Int.[a]
		1658	0			1671	1			1682	3			1636	3
1630	100	1641	31	1633	100	1647	56	1637	100	1652	52	1624[c]	49	1622	14
1585	90	1602	100	1599	48	1611	100			1615	5	1578	100	1562	100
		1579	0	1590	27	1597	65	1607	33	1611	100	1555	16	1543	2
		1562	0			1579	27	1595	23	1596	62	1532	6	1515	6
1553	55	1561	54	1566	99	1568	37			1577	1			1510	9
		1444	0			1440	1			1429	0			1435	0
		1430	2			1412	4	1409	58	1399	23			1412	0
1342	47	1339	9	1342	9	1343	14	1346	37	1346	17			1330	0
		1301	0	1291	46	1291	26			1289	1			1326	2
1267	87	1279	37	1258	44	1264	30	1246	11	1248	17			1294	1
		1276	0			1251	0			1232	0	1278	46	1286	10
		1134	0			1131	17	1145	33	1134	32			1138	5
1127	26	1123	13	1125	34	1128	15			1121	1			1101	4
		1046	0	1080	11	1070	8			1088	0			1087	0
		1046	0	1053	7	1044	7	1047	20	1043	21			1019	1
872	52	863	24	877	55	871	26			874	1			812	9
		859	0			847	0			871	0			806	0
827	6	817	2			821	2	844	74	835	43			780	0
		778	0			800	15			823	9			778	7
		777	0			783	2			806	3			748	0
		730	1			723	1			722	0			734	0
		725	0			708	1			705	15			729	2
		708	0			679	1			677	1			724	0

[a] Intensity of the strongest band is defined as 100.
[b] A scaling factor of 0.98 is used.
[c] May be overlapped with a band of H_2O in matrix.

and 844 cm^{-1} were found to increase more strongly by UV30 irradiation than by UV 32 irradiation. These bands, shown in Fig. 4d, were assigned to Isomer C.

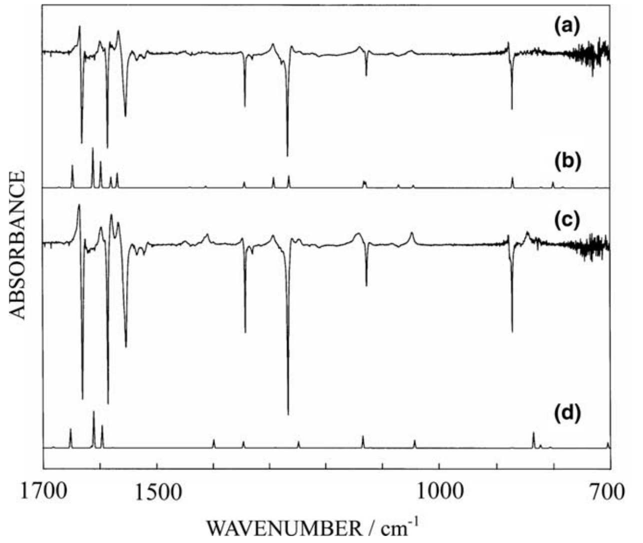


Fig. 4. IR spectral changes due to H-atom migration in DCD: (a) difference between the spectra measured before and after UV irradiation through a UV32 optical filter ($\lambda > 310$ nm) for 2 min; (b) calculated spectral pattern of Isomer B; (c) difference between the spectra measured before and after UV irradiation through a UV 30 optical filter ($\lambda > 290$ nm) for 2 min subsequently to the UV32 irradiation; (d) calculated spectral pattern of Isomer C.

To clarify the origin of this wavelength dependence of the spectral changes and to identify the other bands for Isomer C, which should exhibit similar behavior to the above three bands, a theoretical difference spectrum (UV30 minus UV32) was calculated, as shown in Fig. 5, where the bands for Isomer A were subtracted computationally. A comparison of the calculated spectral patterns, shown in Fig. 5b for Isomers B (down) and C (up), with the observed patterns evidences that Isomer C increased and B decreased when the UV wavelength was changed from $\lambda > 310$ to >290 nm. From these spectral changes, we were able to make separate assignments of the bands of Isomers B and C. The observed and calculated wavelengths and their relative intensities of these isomers are summarized in Table 2. It is concluded that single hydrogen-atom inversion in DCD can occur upon UV irradiation as in 1,2-diiminobenzene [7,8], because Isomer B is now clearly identified. Though Isomer C is also identified, it is still unclear whether it is produced from Isomer A by a direct pathway of double hydrogen-atom inversion or from Isomer B by single hydrogen-atom inversion. If electronically excited states for Isomers A, B, and C are common, the single and double hydrogen-atom inversion may both be feasible in DCD.

There remain a few strong unassigned bands in the observed difference spectrum in Fig. 5a, besides those assigned to Isomers B and C, such as 1578 and 1278 cm^{-1}.

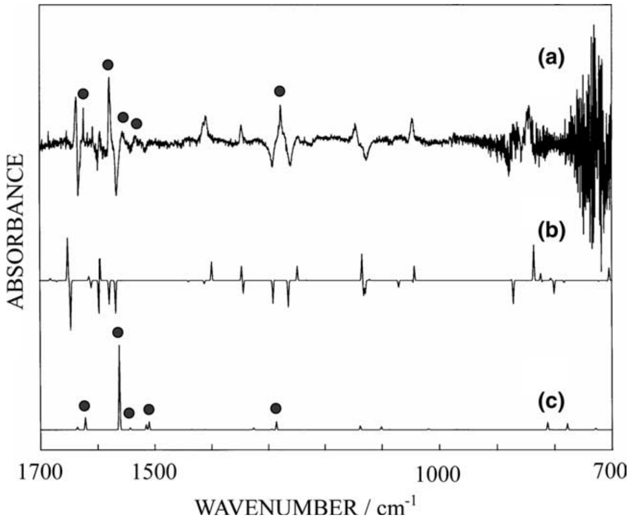


Fig. 5. Wavelength dependence of spectral changes: (a) difference between Fig. 4a and c, where the bands of Isomer A are cancelled computationally; (b) calculated spectral pattern of Isomer B (down) and Isomer C (up); (c) Isomer E, which corresponds to the observed bands marked with a closed circle in (a).

It is possible to assign them to Isomer E by a comparison with the calculated bands, marked with closed circles in Fig. 5c. Isomer E is an intermediate produced by single hydrogen-atom transfer from the amino to the imino group within an intramolecular hydrogen bond, but the stability under our matrix-isolation condition seems to be sufficient to render its IR spectrum observable. The observed and calculated wavenumbers and their relative intensities are summarized in Table 2.

We note, however, that double hydrogen-atom transfer from the amino to the imino group in DCD in the argon matrix cannot be ruled out, because the produced isomer is identical to the original Isomer A, resulting in no IR spectral change with isomerization. Such double hydrogen-atom transfer may be confirmed by deuteration of one the hydrogen atoms in the amino group or by substitution with a methyl group.

4. Conclusion

The IR spectra of DCD measured after deposition is assigned to Isomer A, which has two intramolecular hydrogen bonds between the amino and imino groups. The spectral changes observed after exposure of the matrix sample to UV irradiation ($\lambda > 310$ nm) can be ascribed to hydrogen-atom migration. The photoproducts bands are assigned to Isomers B and C formed by single and double hydrogen-atom inversions around the C═N bonds, respectively, and to Isomer E produced by a single hydrogen-atom transfer from the amino to the imino group within the intramolecular hydrogen bond. Though the spectrum of Isomer B resembles that of Isomer C, they are distinguishable using a shorter wavelength ($\lambda > 290$ nm). These observations lead to the conclusion that single hydrogen-atom inversion and single hydrogen-atom transfer occur in DCD upon UV irradiation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.cplett.2005.04.096.

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