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

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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.

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

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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

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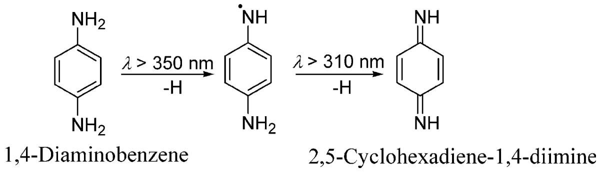
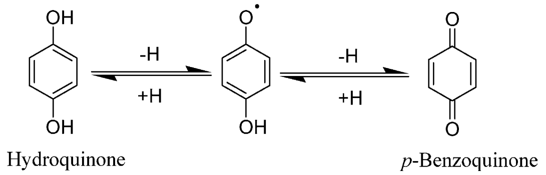


Scheme 1.



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 photoreaction 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-diaminobenzene (purity > 98%) and 4,5-dimethyl-1,2-diaminobenzene (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-diaminobenzene 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].

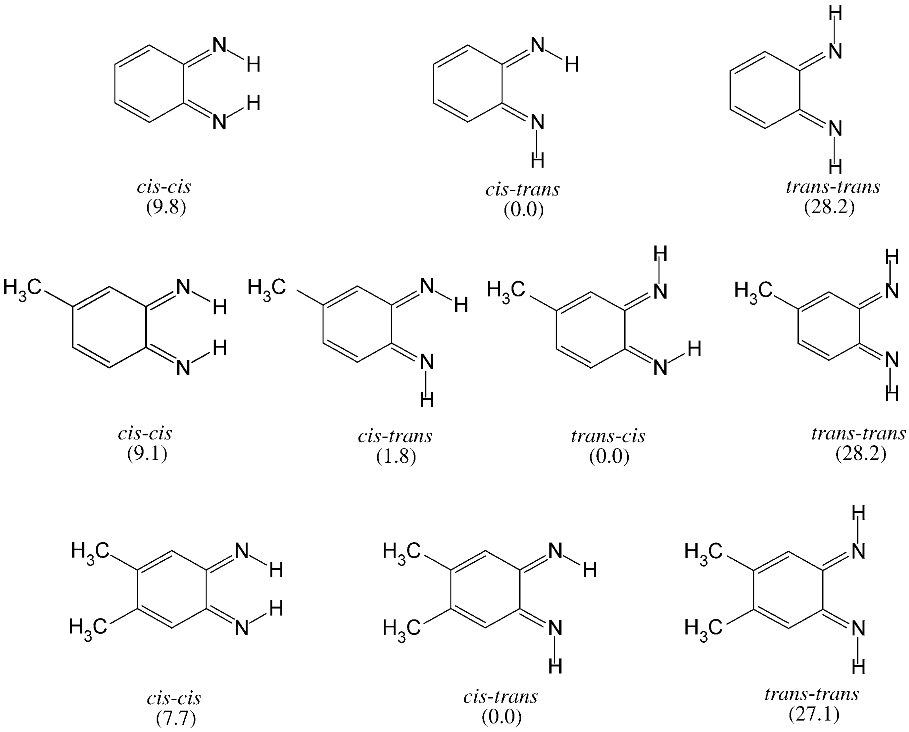


Fig. 1. Possible isomers for 3,5-cyclohexadiene-1,2-diimine, 4-methyl-3,5-cyclohexadiene-1,2-diimine and 4,5-dimethyl-3,5-cyclohexadiene-1,2-diimine. The numbers in parentheses represent relative energies in units of kJ mol^{-1} obtained by DFT/B3LYP/6-31++G** calculation.