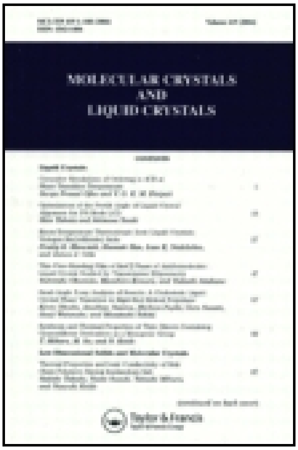

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Transition State Structures of Thermal *Cis-Trans* Isomerization Reaction of Azobenzenes

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Density functional calculations (B3LYP/6–31G*) have been carried out to investigate the transition state structure for the inversion mechanism in the thermal *cis-trans* isomerization reaction of azobenzene and 4-amino-4′-nitroazobenzene. Four and eight conformations were optimized in order to find the inversion transition state of azobenzene and 4-amino-4′-nitroazobenzene, respectively. As a result, it is found that azobenzene and 4-amino-4′-nitroazobenzene have only one genuine inversion transition state, respectively. The inversion barrier of 4-amino-4′-nitroazobenzene is smaller than that of azobenzene. The dipole moment of the inversion transition state of 4-amino-4′-nitroazobenzene is extremely large compared to those of the *cis* and *trans* structures.

Keywords: Azobenzene; Thermal *cis-trans* isomerization; Inversion transition state; Density functional theory calculation

Introduction

Two mechanisms have been proposed for thermal *cis-trans* isomerization reaction of azobenzenes. One is the rotation about the N=N bond and the other is the inversion about one of the N atom via linear transition state (TS). There are numerous experimental and theoretical investigations of the thermal isomerization processes of azobenzenes (see references cited in refs. 1 and 2). It is considered that azobenzene isomerizes via inversion mechanism, while the isomerization of push-pull-azobenzene in polar solvent proceeds via rotation mechanism. The acceleration of the thermal *cis-trans* isomerization for push-pull-azobenzene in polar solvent has been explained by the rotation mechanism, because the rotation TS of push-pull-azobenzene is supposed to have a highly polar zwitterionic structure.

Ab initio calculations of the inversion and rotation TS for thermal *cis-trans* isomerization reaction of azobenzenes have recently reported by Cimiraglia et al.[1,2] They evaluated the correlation energy at the variation-perturbation scheme using the HF/3-21G optimized geometries. According to their results, the inversion mechanism is preferred in most cases, although the energy of the rotation TS is relatively close to that of inversion TS; and in push-pull-azobenzenes, the rotation TS is more stable.

In this study, we focus on the inversion TS structures of azobenzene and 4-amino-4'-nitro-azobenzene. The TS's were optimized by the density functional theory (DFT). The polarized basis set 6-31G* were used, because the 3-21G basis set has some deficiencies for calculating nitrogen-containing molecules; e.g., it tends to give the planar geometry for ammonia.

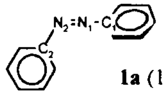
Computational Methods

Geometry optimization of the *cis* and *trans* forms and the corresponding inversion TS has been carried out at the DFT method. The DFT method employed in this study is Becke's three-parameter hybrid model[3] using the Lee-Yang-Parr correlation functional[4] (B3LYP) with 6-31G* basis set[5]. The DFT computations were carried out by the Gaussian 98 program package[6]. Relative energies corrected with zero-point energy are calculated using the *cis* isomer as a reference.

Results and Discussion

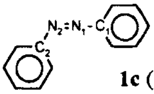
Although Cimiraglia et al.[1,2] assumed that two and four conformations are possible for the inversion TS structures of azobenzene and 4-amino-4'-nitroazobenzene, respectively, four and eight distinguishable conformations are conceivable in these cases (see Figure 1). Therefore, we have examined all possibilities. Figure 1 shows the relative energies and the dipole moments of the inversion TS's at the B3LYP/6-31G* level. The Hessian index, which is the number of imaginary frequencies, is also given in Figure 1. The **1a** and **2a1** are the genuine inversion TS, because they have only one imaginary frequency.

In the **1a** and **2a1**, two benzene rings are perpendicular to each other with collinearity of the N_2=N_1-C_1 bonds. For 4-amino-4'-nitroazobenzene, the inversion proceeds via an azo nitrogen atom attached to the nitrobenzene. The N_1=N_2 bond lengths of the genuine inversion TS's (1.226 Å in **1a** and 1.228 Å in **2a1**, respectively) are shorter than those of *trans* and *cis* forms (1.249 and 1.261 Å in azobenzene, and 1.268 and 1.254 Å in



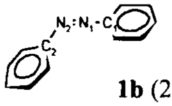
1a (1, 424*i* cm^{-1})

ΔE= 100.73 kJ mol^{-1}
μ = 3.20 D



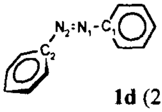
1c (2)

ΔE= 133.31 kJ mol^{-1}
μ = 2.48 D



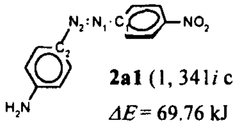
1b (2)

ΔE= 129.05 kJ mol^{-1}
μ = 2.15 D



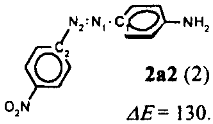
1d (2)

ΔE= 154.86 kJmol^{-1}
μ = 3.17 D



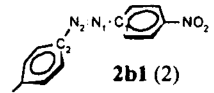
2a1 (1, 341*i* cm^{-1})

ΔE= 69.76 kJ mol^{-1}
μ = 13.41 D



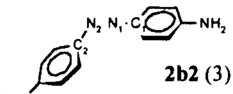
2a2 (2)

ΔE= 130.89 kJ mol^{-1}
μ = 4.24 D



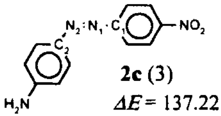
2b1 (2)

ΔE= 115.89 kJ mol^{-1}
μ = 9.34 D



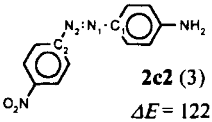
2b2 (3)

ΔE= 159.39 kJ mol^{-1}
μ = 5.15 D



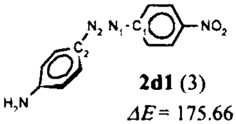
2c (3)

ΔE= 137.22 kJmol^{-1}
μ = 8.04 D



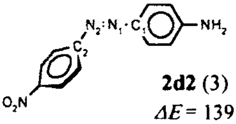
2c2 (3)

ΔE= 122.50 kJ mol^{-1}
μ = 10.42 D



2d1 (3)

ΔE= 175.66 kJ mol^{-1}
μ = 4.51 D



2d2 (3)

ΔE= 139.66 kJ mol^{-1}
μ = 10.46 D

Figure 1. The relative energies (ΔE) and the dipole moments (μ) of the inversion transition states at the B3LYP/6-31G* level. Numbers in parenthesis refer to Hessian index. Imaginary frequencies are also shown in parenthesis for true TS (**1a** and **2a1**).

4-amino-4'-nitroazobenzene, respectively). Similarly the N_1-C_1 bonds (1.335 Å in **1a** and 1.317 Å in **2a1**, respectively) are shorter than those of *trans* and *cis* forms (1.436 and 1.419 Å in azobenzene, and 1.414 and 1.423 Å in 4-amino-4'-nitroazobenzene, respectively). The perpendicular orientation of two benzene rings may be ascribed to the competition between two perpendicular π-conjugations as proposal by Cimiraglia et al.[2]: one is conjugation between the coplanar azo and benzene ring, the other is conjugation between the p_z lone pair orbitals of the *sp*-hybridized nitrogens and the phenyl ring.

The inversion barrier of 4-amino-4'-nitro derivative (69.8 kJ mol^{-1}) is smaller than that of the unsubstituted azobenzene (100.7 kJ mol^{-1}). This is qualitatively consistent with the experimental data in gas phase for 4-dimetylamino-4'-nitroazobenzene and azobenzene (102 and 118 kJ mol^{-1}, respectively).[7, 8]

The dipole moment of the inversion TS of azobenzene (3.20 D) is the same as that of *cis*-azobenzene (3.22 D), while the dipole moment of the inversion TS of push-pull-azobenzene (13.41 D) is extremely large compared to those of the *cis* and *trans* isomers (7.51 and 9.82 D, respectively). This result is particularly surprising in view of the fact that the acceleration of *cis-trans* isomerization of push-pull-azobenzene in polar solvent may be explained by the inversion mechanism solely, i.e., without taking account of the rotation mechanism. However, we need information on the rotation mechanism at the same level of calculation. Further investigations are in progress.

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