Ab Initio Molecular Orbital and Density Functional Studies on the Stable Structures and Vibrational Properties of *trans*- and *cis*-Azobenzenes

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The structure of *trans*-azobenzene (TAB) has been a subject of controversy in experimental and theoretical studies. To provide the theoretical basis for stable structures and vibrational properties of TAB and *cis*-azobenzene (CAB), we performed ab initio molecular orbital calculations based on the second-order Møller−Plesset (MP2) method and density functional theory (DFT). Only the MP2 calculation accounting for the diffuse basis set (6-31+G*) leads to the distorted structure of TAB, which is consistent with the gas-phase electron diffraction experiment. The Hartree−Fock and DFT (PW91PW91, MPW91, BP86, and B3LYP) calculations, on the other hand, result in the almost planar structure of TAB. The frequencies of normal modes of TAB and CAB are calculated most accurately by the PW91PW91/6-31+G* method followed by the BP86/6-31G* method. These results are expected to provide useful benchmark data on the accuracy of MP2 and DFT methods for describing the structural and vibrational properties of azobenzene-like molecules, which consist of weakly interacting phenyl rings.

1. Introduction

Azobenzene is one of the typical aromatic molecules having unique photochromic properties. It has two stable *trans*- and *cis*-conformations, and its photoinduced isomerization between the two conformations has found wide applicability in reversible optical data storage. Recently, numerous experimental studies have concentrated on clarifying the mechanism of the photoinduced isomerization. [1] Azobenzene is also attracting attention as a core part of dendrimers, which are nanosized hyperbranched macromolecules with a regular tree-like structure.[2] In the experiment by Jiang and Aida,[3] a large aryl ether azodendrimer with an azobenzene core was found to undergo cis-to-trans isomerization upon exposure to weak infrared (IR) light.

It is necessary to determine the stable structures of *trans*- and *cis*-azobenzenes to clarify the mechanism for isomerization and associated photochromism. However, in experimental studies the structure of *trans*-azobenzene (TAB) has been a subject of controversy for decades. X-ray diffraction (XRD) experiments[4] suggested that the TAB molecules are very slightly distorted from planarity, whereas gas-phase electron diffraction (ED) experiments[5] showed that the phenyl rings of TAB are twisted by as much as 30° around the N═N−C plane. Raman measurements[6] on TAB and its isotopically substituted derivatives suggested that TAB has a distorted structure with C_i symmetry in solution. Therefore, the twist angle of phenyl rings in TAB has not yet been determined completely by experiments. Regarding the structure of *cis*-azobenzene (CAB), the XRD study[7] suggested a nonplanar structure consisting of a 2-fold axis of symmetry with the phenyl rings rotated by 53.3 °around the N═N−C plane.

To provide the theoretical basis for stable structures and vibrational properties of TAB and CAB, ab initio molecular orbital (MO) calculations based on the second-order Møller−Plesset (MP2) method and density functional theory (DFT) have been carried out.[8,9] The MP2 calculation for TAB[8] using the combined basis set 6-31G$^\alpha$, in which the basis set for nitrogens was changed to 6-31+G(d) and carbon and hydrogen atoms were treated with the 6-31G basis set, led to the result that TAB has a planar structure with C_{2h} symmetry and two imaginary vibrational frequencies and that some of the vibrational assignments do not match the experimental data. This result seems to come from the unbalanced nature of the 6-31G$^\alpha$ basis set adopted. On the other hand, the DFT calculations utilizing the 6-31G* basis set[9] for TAB and CAB improved the assignments of vibrational modes. However, there was given no explicit value of the twist angle of the phenyl ring in TAB, which is a main subject of controversy in the experimental studies. Therefore, the structure of TAB has not yet been described satisfactorily by the theoretical studies based on MO methods.

We believed that it is indispensable to obtain accurate stable structures of TAB and CAB for investigating their vibrational properties and the isomerization mechanism. As a result, the following steps were taken in the present study: (1) Obtain stable structures of TAB and CAB by high-level MO methods such as MP2 and DFT with a large and diffuse basis set. (2) Perform the normal-mode analysis for the obtained structures. From these calculations, we would obtain benchmark data on the accuracy of these state-of-the-art MO calculations. We also performed some semiempirical MO calculations and tested their accuracy and efficiency for investigating the structural and vibrational properties, because one of our goals[10] is to elucidate the IR-induced isomerization mechanism of the large azodendrimers.[3]

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2. Details of Molecular Orbital Calculations

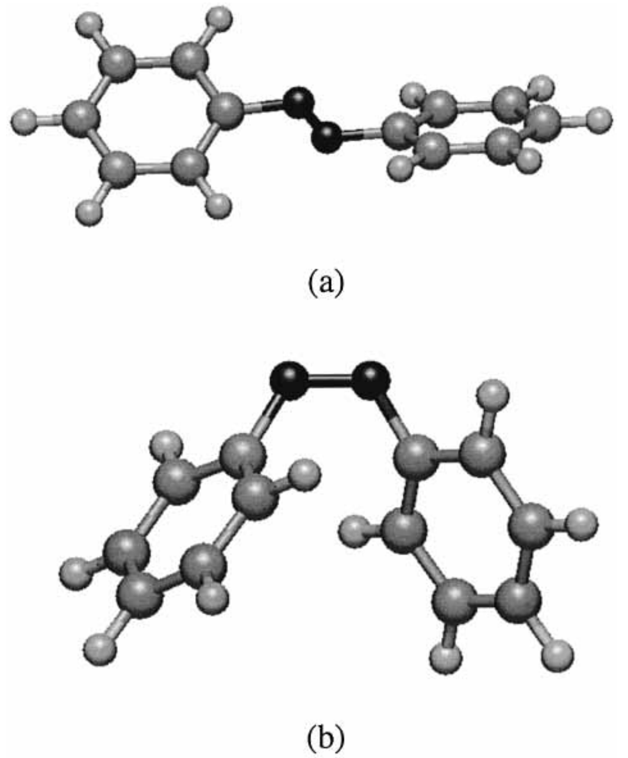
The ab initio HF and MP2 as well as DFT calculations for optimizing the structures of TAB and CAB were carried out using the GAUSSIAN 98 (G98)[11] (DEC-AXP−OSF/1, Rev. A.1) program package. We employed the five DFT functionals: (1) PW91PW91 (the Perdew-Wang91 functionals[12,13] for the exchange and the correlation parts), (2) MPW91 (the modified Perdew-Wang91 exchange[14] plus the Perdew-Wang91 correlation[12,13] functionals), (3) B3LYP (Becke's three-parameter hybrid method[15] using the LYP correlation functional[16]), (4) BP86 (Becke's 1988 exchange functional[17] combined with the gradient-corrected correlation function of Perdew[18]), and (5) SVWN5 (local spin density approximation by Slater[19] combined with the correlation function of Vosko, Wilk, and Nusair[20]). The accuracy of the DFT methods is essentially limited by the accuracy of the exchange and correlation functionals used in the calculation. In our previous study[21] on the conformations of 1,2-diphenylethane, the PW91PW91[12,13] and MPW91[12−14] functionals were used because these functionals reduce the overestimated error of the local density approximation in bond energy and because they have no adjustable parameter for the exchange functional. In the present study, we also used both the functionals, and the other three functionals were used as well for comparing our results with those by Biswas and Umapathy.[9] Furthermore, for the purpose of estimating the effect of basis sets on the stable structures of TAB and CAB, we tested the four types of basis sets: 6-31G*, 6-31G**, 6-311G**, and 6-31+G*. It is noted that the choice of basis set is critical for obtaining stable structures and that the 6-31+G* basis set, including diffuse functions, is essential for accurately describing the interaction between the two phenyl rings in TAB, as will be shown in the next section.

The semiempirical MO calculations using the MOPAC2000 program package[22] were additionally carried out with the MNDO, AM1, and PM3 Hamiltonians. The accuracy of these methods was tested through the comparison with the MP2 and DFT results.

To clarify the vibrational properties obtained by the IR and Raman experiments as well as the isomerization dynamics between TAB and CAB, a detailed analysis of the normal coordinates is required. We evaluated the vibrational frequencies and its corresponding eigenvectors of TAB and CAB by the HF/6-31+G*, MP2/6-31G*, PW91PW91/6-31+G*, MPW91/6-31+G*, B3LYP/6-31+G*, BP86/6-31G*, SVWN5/6-31G**, and semiempirical PM3 methods.

3. Results and Discussion

3.1. Stable Structures of *trans*- and *cis*-Azobenzenes. The structure of TAB has been a subject of controversy in experimental as well as theoretical studies. The XRD result[4] suggested a slightly distorted but nearly planar structure, whereas the gas ED study[5] showed that the phenyl ring is twisted by 30° around the N═N−C plane. The several DFT and HF calculations using the 6-31G* basis set[9] showed a slightly distorted structure with C_i symmetry, although the value of the twist angle of the phenyl ring was not shown explicitly. On the other hand, the MP2 calculation with the combined $6\text{-}31G^{\alpha}$ basis set[8] resulted in a planar structure with C_{2h} symmetry. The present results for the stable structures of TAB and CAB, which have been obtained by the MP2/6-31+G* calculations, are shown in Figure 1a and 1b, respectively. The most remarkable difference between the present and previous results is the twist angle of the phenyl rings around the N═N−C plane for TAB. As shown in Figure 1a, TAB has a rather distorted structure from a plane, with a twist angle of 18.5°. The optimized structural parameters for TAB, that is, the bond lengths, bond angles, and dihedral angles, are presented in Table 1 along with those obtained by experiments[4,5] and by the previous calculations.[8,9]


(a)

(b)

Figure 1. Stable structures of (a) *trans*-azobenzene and (b) *cis*-azobenzene obtained by MP2/6-31+G* calculations. Note that the phenyl rings in *trans*-azobenzene are rotated by 18.5° with respect to the N═N−C plane.

A noteworthy value in Table 1 is the dihedral angle N═N−C−C, which is the averaged value of the two kinds of twist angles of phenyl rings around the N═N−C plane and is a main point of controversy. In the gas ED experiment,[5] it was not possible to decide whether the phenyl rings are twisted in the same direction (C_2 symmetry) or in the opposite direction (C_i symmetry). All of the present calculations show that the phenyl rings prefer to rotate in the opposite direction, as shown in Figure 1a, and the stable structure of TAB has the C_i symmetry. However, the calculated value of this dihedral angle is significantly dependent on the MO methods as well as the basis sets.

To obtain the accurate value of this dihedral angle, we investigated its dependence on the basis set, because we considered that the choice of basis set is critical and that the basis sets utilized in the previous calculations[8,9] are not sufficient for describing the long-range interaction between the two phenyl rings in TAB. At first, the HF and MP2 optimizations were performed with three basis sets: 6-31G**, 6-311G**, and 6-31+G*. The last one includes the diffuse functions for both the nitrogen and carbon atoms. Only the MP2/6-31+G* calculation, which should be the most accurate among all the present calculations, resulted in the distorted structure (Figure 1a), in which the phenyl rings are significantly twisted by 18.5° around the N═N−C plane. This calculated value of the N═N−C−C angle is comparable to that (27.9°) of the molecule with C_i symmetry obtained by the gas ED experiment.[5] This result was reproduced irrespective of the initial structure, planar or nonplanar. Second, to test the efficiency of the DFT methods, the structure was optimized by several DFT methods. The SVWN5/6-31G**, BP86/6-31G*, and B3LYP/6-31G** results

TABLE 1: Structural Data for *trans*-Azobenzene Obtained from Experiments and Molecular Orbital Calculations[a]

	N=N	C−N	N=N−C	N−C−C	C−N=N−C	N=N−C−C
Semiempirical Calculations						
MNDO	1.230	1.437	116.9	124.8, 115.4	0.2	35.2[h]
AM1	1.231	1.437	119.6	125.0, 116.0	0.7	15.3[h]
PM3	1.231	1.447	119.8	124.2, 115.5	0.2	13.7[h]
DFT Calculations						
SVWN5/6-31G**	1.265	1.400	114.3	124.0, 115.7	0.0	0.0[h]
BP86/6-31G*	1.279	1.421	114.0	125.0, 115.2	0.0	0.0[h]
B3LYP/6-31G**	1.261	1.419	114.8	124.8, 115.3	0.0	0.0[h]
B3LYP/6-31+G*	1.258	1.420	115.3	124.7, 115.3	0.0	0.0[h]
PW91PW91/6-31+G*	1.273	1.418	114.7	124.9, 115.3	0.0	0.1[h]
MPW91/6-31+G*	1.251	1.413	115.0	124.6, 115.4	0.0	0.1[h]
HF & MP2 Calculations						
HF/6-31G**	1.220	1.421	115.7	124.4, 115.5	0.0	0.0[h]
HF/6-31+G*	1.218	1.422	115.9	124.4, 115.5	0.0	0.1[h]
MP2/6-31G**	1.280	1.422	113.5	124.8, 114.8	0.0	0.1[h]
MP2/6-311G**	1.272	1.421	113.6	124.8, 115.3	0.0	0.0[h]
MP2/6-31+G*	1.279	1.423	113.4	124.0, 115.3	2.4	18.5[h]
Experiments						
Gas E.D. (C_2 symmetry)[b]	1.259	1.420	116.0	121.2	0.0[f]	30.1
Gas E.D. (C_i symmetry)[b]	1.268	1.427	114.5	123.0	0.0[f]	27.9
X-ray diffraction (A site)[c]	1.247	1.428	114.1	123.7, 115.6	0.0[f]	16.7
X-ray diffraction (B site)[c]	1.245	1.428	113.9	124.2, 115.8	0.0[f]	6.8
Previous Calculations						
MP2/6-31G$^{\alpha}$[d]	1.275	1.431	−[g]	−[g]	0	0
B3LYP/6-31G*[e]	1.260	1.418	114.7	124.7, 115.3	−[g]	−[g]

[a] Units: bond lengths (Å), valence and dihedral angles (degrees). [b] Ref 5. [c] Ref 4. [d] Ref 8. [e] Ref 9. [f] Assumed value. [g] Values not reported in the original articles. [h] Averaged values.

are nearly identical to the previous DFT results.[9] We then added diffuse functions in the B3LYP calculation, expecting that the phenyl rings would twist each other. However, the angle N=N−C−C was still found to be almost 0°. This trend is also observed for the PW91PW91 and MPW91 results, as shown in Table 1. Therefore, we concluded that the correction for the electron correlation energy by MP2 as well as the diffuse basis set 6-31+G* are essential to obtain the distorted structure of TAB, which is comparable to that in the gas ED experiment.[5] The previous calculations[8,9] using the 6-31G* or 6-31G$^{\alpha}$ basis set seem to fail to reproduce the experimental structure because of the insufficiency of the basis sets employed.

We considered the reason why the phenyl rings of TAB are significantly twisted only in the MP2/6-31+G* calculation as follows. The conformation of TAB is mainly determined by the $\pi-\pi$ and n$-\pi$ interactions of the azo group with the phenyl rings and the repulsive interaction of the ortho hydrogens of the phenyl ring with the lone-pair electrons of the distal nitrogen. The π-π interaction makes the planar conformation more stable, whereas the n$-\pi$ and the repulsive interactions make the nonplanar conformation more preferable than the planar one. It can be predicted from the present MP2 results that the calculations with the 6-31G** and 6-311G** basis sets underestimate the n$-\pi$ and repulsive interactions, providing the stable planar structure. On the other hand, by using the diffuse basis set 6-31+G*, the lone-pair electrons of the nitrogen atoms are described accurately to be more delocalized, so that the n$-\pi$ and repulsive interactions are estimated with sufficient accuracy, resulting in the twisted conformation of TAB. There is also a repulsive interaction between the ortho hydrogens of two phenyl rings. By adding diffuse functions to the basis set of hydrogen atoms, this repulsive interaction may be described more accurately, so that the twist angles of the phenyl rings are enhanced, resulting in the calculated N=N−C−C angle becoming more comparable to the value of the gas ED experiment.[5]

It is also noted in Table 1 that the value of the C−N=N−C dihedral angle must be considered carefully. Only the MP2/6-31+G* calculation shows that the C−N=N−C group is not planar, whereas the experimental studies[4,5] assumed the coplanarity of this group. To investigate the effect of this nonplanarity, we reoptimized the TAB structure by fixing the C−N=N−C angle to be 0° by the MP2/6-31+G* method. The optimized N=N−C−C angle was found to be almost 0°, although the bond lengths and valence angles shown in Table 1 were almost the same as the results of full optimization. This result indicates that the small change in the C−N=N−C angle causes the large twist of phenyl rings and that this angle must be examined more carefully in experiments.

Regarding the bond length of N=N, it is elongated about 0.06 Å due to the inclusion of the electron correlation by MP2, and the value (1.279 Å) in the MP2/6-31+G* calculation compares well with that (1.268 Å) for the molecule with C_i symmetry obtained by the gas ED experiment.[5] On the other hand, the C−N bond is almost the same in the HF and MP2 methods and agrees with the experiments within the 0.006-Å difference. All DFT calculations except for MPW91/6-31+G* provide the N=N and C−N bond lengths comparable to the experimental ones, although the N=N−C−C angle cannot be well described by the DFT methods. The semiempirical calculations yield rather distorted structures, which are comparable to the experimental structure, although the N=N bond length is underestimated by about 0.04 Å.

In the same way as TAB, the structure of CAB was investigated by several MO methods. The stable structure obtained by the MP2/6-31+G* calculation is shown in Figure 1b, and the optimized structural parameters are presented in Table 2 along with those obtained by the XRD experiment for the CAB crystal[7] and by the BP86/6-31G* calculation.[9] The DFT, HF, and MP2 calculations provide values of the dihedral angles C−N=N−C and N=N−C−C that are comparable to those obtained by the XRD experiment, although the calculated bond lengths show rather large differences (at most 0.036 Å) compared to the experimental values. The main reason for these discrepancies may be ascribed to the crystal-field effect on the

TABLE 2: Structural Data for *cis*-Azobenzene Obtained from Experiments and Molecular Orbital Calculations[a]

	N═N	C−N	N═N−C	N−C−C	C−N═N−C	N═N−C−C
Semiempirical Calculations						
MNDO	1.210	1.447	126.8	119.7, 119.7	0.0	86.2[d]
AM1	1.204	1.442	129.2	122.5, 118.0	2.3	45.8[d]
PM3	1.216	1.453	126.9	120.2, 118.8	0.0	79.9[d]
DFT Calculations						
SVWN5/6-31G**	1.252	1.410	123.4	122.8, 116.6	13.0	40.5[d]
BP86/6-31G*	1.264	1.438	124.0	123.1, 116.3	12.0	42.5[d]
B3LYP/6-31G**	1.249	1.436	124.0	123.0, 116.4	9.8	45.8[d]
B3LYP/6-31+G*	1.249	1.437	124.1	122.9, 116.5	9.6	46.2[d]
PW91PW91/6-31+G*	1.261	1.434	123.9	122.9, 116.4	11.7	43.2[d]
MPW91/6-31+G*	1.242	1.428	123.6	122.8, 116.5	9.1	46.5[d]
HF & MP2 Calculations						
HF/6-31G**	1.217	1.434	123.9	122.6, 116.7	5.1	54.0[d]
HF/6-31+G*	1.217	1.434	123.9	122.6, 116.8	4.9	54.6[d]
MP2/6-31G**	1.272	1.438	121.0	122.1, 116.7	7.2	50.0[d]
MP2/6-311G**	1.266	1.438	120.6	122.1, 116.9	6.5	50.6[d]
MP2/6-31+G*	1.274	1.440	120.4	122.0, 116.8	6.4	52.2[d]
Experiment						
X-ray diffraction[b]	1.253	1.449	121.9	122.5, 117.3	8.0	53.3
Previous Calculation						
BP86/6-31G*[c]	1.264	1.437	123.9	123.1, 116.3	12.0	47.4

[a] Units: bond lengths (Å), valence and dihedral angles (degrees). [b] Ref 7. [c] Ref 9. [d] Averaged values.

TABLE 3: Relative Stability of the *trans*- and *cis*-Azobenzenes Estimated with the B3LYP, PW91PW91, MPW91, HF, and MP2 Methods

method/basis set	total energy (hartree) *trans*	total energy (hartree) *cis*	relative energy (kcal/mol)
DFT Calclulations			
B3LYP/6-31+G*	−572.78430	−572.75907	−15.8
PW91PW91/6-31+G*	−572.56549	−572.54301	−14.1
MPW91/6-31+G*	−572.63829	−572.61410	−15.2
HF & MP2 Calculations			
HF/6-31+G*	−569.11736	−569.08880	−17.9
MP2/6-31G**	−569.11111	−569.08295	−17.7
MP2/6-311G**	−569.21230	−569.18277	−18.5
MP2/6-31+G*	−569.10808	−569.07894	−18.3

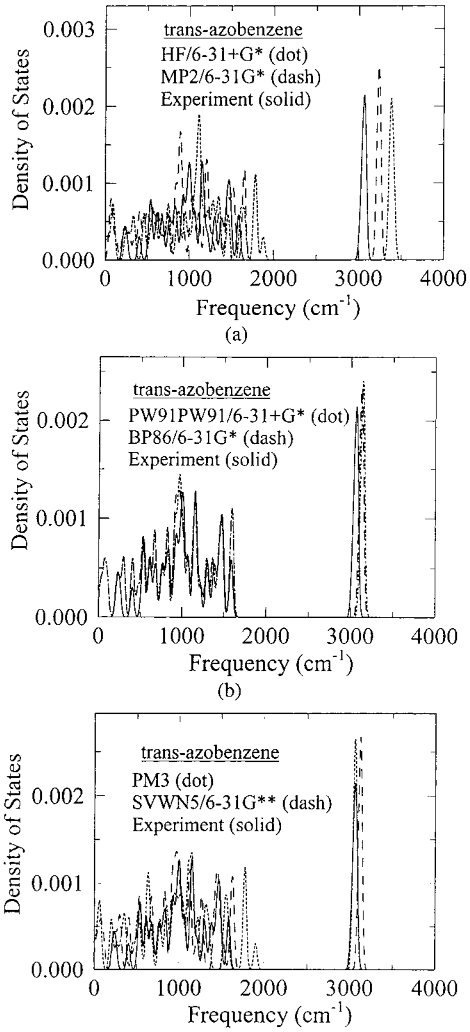
CAB molecules. From the comparison between the XRD and MP2/6-31+G* results, this effect can be estimated as the N═N bond being shortened by 0.021 Å, whereas the C−N bonds are elongated by 0.009 Å. Compared with the previous BP86/6-31G* results,[9] the present BP86/6-31G* calculation reproduces the previous results except for the N═N−C−C angle. It is noted that we obtained 42.5°from the average of the two values, 37.5°and 47.6°, and the latter value is nearly equal to the 47.4°obtained by the previous calculation. Therefore, the present results for CAB are in reasonable agreement with the values obtained by the XRD experiment[7] and the DFT calculation.[9]

In the case of TAB, the interaction between the two phenyl rings is accurately described only by the MP2 method with the diffuse basis set 6-31+G*. On the other hand, this interaction in CAB is reasonably described also by the HF and DFT methods, as seen for the values of the dihedral angle N═N−C−C in Table 2. We considered that the distance between the two phenyl rings of CAB is much shorter than that of TAB, as shown in Figures 1a and 1b, so that the interaction between them is more appropriately described by the HF or DFT methods with nondiffuse basis sets such as 6-31G* and 6-31G**.

The comparison of the values in Tables 1 and 2 clarifies the relation between electronic and structural properties of TAB and CAB. Because CAB is completely nonplanar, the π electrons prefer to localize on the N═N bond compared to the large π-conjugation in TAB. As a result, it is expected that the N═N bond in CAB is shorter than that in TAB and that the C−N bonds in CAB are longer than those in TAB. All the calculations in the present study show this trend. The values of the N═N−C angle (113.4 and 120.4° for TAB and CAB, respectively) indicate that the nitrogen atoms in CAB have more sp$_2$ character than those in TAB. The most remarkable difference between TAB and CAB is the N═N−C−C dihedral angle, which is the twist angle of the phenyl rings around the N═N−C plane. In the CAB conformation (Figure 1b), the hydrogen atoms of each of the phenyl groups exist at a shorter distance than those in TAB, so that the phenyl rings in CAB are twisted more significantly to decrease the repulsive interaction between the hydrogen atoms. In the analysis of the isomerization process between TAB and CAB, the relative position of the phenyl rings, as well as the structure of the C−N═N−C group, is essential. Therefore, the MP2/6-31+G* method is expected to be accurate enough to investigate this isomerization mechanism.

The total energies and relative stability of TAB and CAB obtained by the DFT, HF, and MP2 methods are presented in Table 3. The total energies were obtained for the fully optimized structures, and the energies relative to the total energies of CAB were evaluated in a kcal/mol unit. The DFT/6-31+G* calculations show that TAB is about 15 kcal/mol more stable than CAB, whereas the HF and MP2/6-31+G* calculations result in the 18 kcal/mol preference of TAB. The dependence of relative energy on the basis set in the MP2 calculations is less than 1 kcal/mol, resulting in a consequence that TAB is about 18 kcal/mol more stable than CAB in a vacuum. An experimental study on the heat of combustion of TAB and CAB[23] indicated that TAB is about 10 kcal/mol more stable than CAB at 25 °C. Therefore, we concluded that the present DFT, HF, and MP2 calculations can describe the relative stability between TAB and CAB with reasonable accuracy.

3.2. Vibrational Properties of *trans*- and *cis*-Azobenzenes. The vibrational properties of TAB and CAB were investigated by Raman[6] and IR[24] experiments as well as by theoretical studies[8,9] based on HF, MP2, and DFT methods. In a previous study by Biswas and Umapathy,[9] BP86/6-31G* was found to be very useful for predicting vibrational frequencies of TAB and CAB, and the assignments of various vibrational modes obtained by the experiment were made reasonably well based on the BP86/6-31G* result. In the present study, we carried

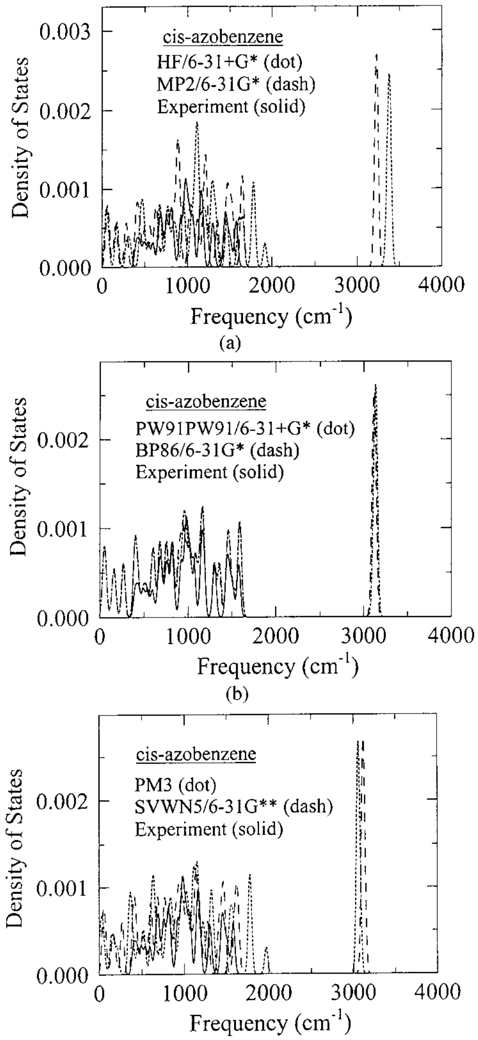


(a)

(b)

(c)

Figure 2. Distribution of the normal-mode frequencies for the *trans*-azobenzene. The density of the states of vibrational modes is obtained by assigning the Gaussian distribution with a 20-cm^{-1} dispersion to each normal mode and normalizing the sum of the contributions from all the normal modes to be unity. The calculated results are compared with experimental results (solid line):[6,24] (a) HF/6-31+G* (dot line) and MP2/6-31G* (dash line), (b) PW91PW91/6-31+G* (dot line) and BP86/6-31G* (dash line), and (c) SVWN5/6-31G** (dash line) and semiempirical PM3 (dot line) calculations.



(a)

(b)

(c)

Figure 3. Distribution of the normal-mode frequencies for *cis*-azobenzene. The details are the same as Figure 2.

out normal-mode analyses for TAB and CAB utilizing the HF, MP2, DFT, and semiempirical MO methods, for the sake of testing the efficiency of these methods for describing the vibrational properties of TAB and CAB. The calculated results are compared with experimental results[6,24] in Figures 2 and 3, in which the density of states (DOS) for the vibrational modes is illustrated. The DOS was obtained by assigning the Gaussian distribution with a 20-cm^{-1} dispersion to each normal mode and normalizing the sum of the contributions from all the normal modes to be unity.

The HF/6-31+G* and MP2/6-31G* results for TAB are compared with the experimental results[6,24] in Figure 2a. It is noted that the 6-31G* basis set was used in the MP2 normal-mode analysis for the optimized structure obtained by MP2/6-31+G*, due to the limitation of the computational resources. The normal-mode analysis for the optimized structure by the MP2/6-31G* method was also carried out, and it was confirmed that the frequencies obtained by both the MP2 analyses agree with each other within the 10-cm^{-1} difference except for the frequency modes lower than 200 cm^{-1}. As shown in Figure 2a, the HF result shifts by at most 320 cm^{-1} to higher frequency compared with experiment, so that the correction for the electron correlation energy is essential for obtaining accurate vibrational frequencies. The MP2 result also shows rather large (about 170 cm^{-1}) shifts to higher frequency. This shift may arise from the incompleteness of the basis set and could be improved by introducing diffuse functions in the basis set.

Among the five DFT results, the PW91PW91/6-31+G* one reproduces the experimental frequencies with the smallest error, with a size of at most 26 cm^{-1}, except for the C$-$H stretching modes at around 3000 cm^{-1}. In previous DFT calculations,[9] the BP86/6-31G* method was found to be the most accurate. The present BP86/6-31G* result reproduces the previous result[9] within the 3-cm^{-1} difference, but it has a larger error (32 cm^{-1}) than the PW91PW91/6-31+G* method, as shown in Figure 2b and Table 4, in which the vibrational frequencies obtained by the present BP86 and PW91PW91 calculations are compared with the experimental results.[6,24] The modes at around a frequency of 3000 cm^{-1}, which are assigned to the C$-$H stretching modes, shift significantly (50$-$80 cm^{-1} in BP86 and 70$-$100 cm^{-1} in PW91PW91) to higher frequency in the present calculations. This large shift seems to arise from the incompleteness of the 6-31G* and 6-31+G* basis set, and the polarization and/or diffuse functions for hydrogen atoms are necessary for

TABLE 4: Frequencies (cm^{-1}) for the Ag and Au Normal Vibrations of *trans*-Azobenzene Obtained by the Experiments[6,24] and by the Present DFT Calculations[a]

experiments		BP86/6-31G*		PW91/6-31+G*	
Ag	Au	Ag	Au	Ag	Au
3085	3081	3144 (59)	3144 (63)	3159 (74)	3159 (78)
3073	3065	3133 (60)	3132 (67)	3148 (75)	3148 (83)
3066	3053	3122 (56)	3122 (69)	3138 (72)	3138 (85)
3060	3036	3112 (52)	3111 (75)	3128 (68)	3128 (92)
3044	3020	3102 (58)	3101 (81)	3118 (74)	3118 (98)
		1604	1602	1606	1603
1595	1585	1588 (−7)	1584 (−1)	1589 (−6)	1585 (0)
1493	1486	1485 (−8)	1480 (−6)	1491 (−2)	1481 (−5)
1473	1456	1465 (−8)	1451 (−5)	1463 (−10)	1451 (−5)
1443	1399	1419 (−24)	1367 (−32)	1431 (−12)	1373 (−26)
1379	1300	1363 (−16)	1299 (−1)	1369 (−10)	1302 (2)
1315	1223	1294 (−21)	1228 (5)	1298 (−17)	1234 (11)
1184	1160	1181 (−3)	1157 (−3)	1185 (1)	1158 (−2)
1158	1152	1157 (−1)	1144 (−8)	1158 (0)	1149 (−3)
1146	1072	1131 (−15)	1074 (2)	1136 (−10)	1078 (6)
1071	1020	1070 (−1)	1017 (−3)	1074 (3)	1019 (−1)
1023	1000	1017 (−6)	986 (−14)	1019 (−4)	987 (−13)
1003	813	985 (−18)	816 (3)	987 (−16)	819 (6)
913	615	912 (−1)	610 (−5)	913 (0)	611 (−4)
670	545	661 (−9)	528 (−17)	663 (−7)	530 (−15)
614	521	604 (−10)	514 (−7)	604 (−10)	515 (−6)
		297	80	299	81
219	985	215 (−4)	962 (−23)	217 (−2)	966 (−19)
968		962 (−6)	941	966 (−2)	950
938	927	941 (3)	912 (−15)	951 (13)	912 (−15)
	850	907	829 (−21)	907	824 (−26)
836	776	830 (−6)	771 (−5)	825 (−11)	768 (−8)
755	689	752 (−3)	679 (−10)	747 (−8)	676 (−13)
	545	673	538 (−7)	669	539 (−6)
		471	401	469	401
403		405 (2)	294	407 (4)	294
251		245 (−6)	58	249 (−2)	59
		106	22	109	22

[a] Values in parentheses are the discrepancies from the experimental frequencies.

obtaining lower frequencies with respect to the C−H stretching modes. Regarding the frequencies of the other modes, both the calculations reproduce the experimental results well. In particular, the N═N stretching A_g modes at 1493 and 1443 cm^{-1} are well described by the PW91PW91/6-31+G* method. The error in frequency is less than 12 cm^{-1}, which is half of that (24 cm^{-1}) obtained by BP86/6-31G*. The N═N stretching modes may play an important role for the cis-to-trans isomerization of azobenzene, so that the PW91PW91/6-31+G* method seems to be more suitable for analyzing the dynamics of this isomerization.

We also compared the results of the local DFT (SVWN5/6-31G**) and semiempirical (PM3) MO calculations with the experiments in Figure 2c. The former has similar frequencies for the C−H stretching modes as the BP86 and PW91PW91 methods, although the frequencies of the N═N stretching modes are about 33 cm^{-1} higher compared with the experiments, indicating that the effect of the nonlocal part of the exchange-correlation energy is considerable for the N═N vibrations. On the other hand, the PM3 result has about 200 cm^{-1} error in the frequencies between 1500 and 2000 cm^{-1}, although the frequencies of the C−H stretching modes at around 3000 cm^{-1} are well described. Therefore, if the semiempirical MO methods are used in the normal-mode analysis for such a large molecule as the azodendrimer,[10] we have to consider that the calculated normal-mode frequencies falling in these regimes may have errors with similar size.

The normal modes of CAB were investigated in the same way as TAB. The calculated DOS's by several MO methods are compared with the IR spectra experiment[24] in Figure 3. (Note that 31 of 66 normal modes are missing in the experimental data.) As shown in Figure 3a, the HF/6-31+G* and MP2/6-31G* results have rather large errors (at most 260 and 70 cm^{-1}, respectively) in frequency compared with experiment. The PW91PW91/6-31+G* and BP86/6-31G* calculations have almost the same accuracy in frequency, as shown in Figure 3b. The maximum difference in frequencies between the corresponding experimental and calculated modes is 19 cm^{-1} in both the calculations. As for the N═N stretching and torsional vibrations with the 1511 and 596 cm^{-1} frequencies in the experiment, the PW91PW91/6-31+G* calculation reproduces these frequencies within the 13-cm^{-1} error, whereas the BP86/6-31G* result differs by at most 12 cm^{-1}. The other DFT calculations show rather large errors in these frequencies: 138 (MPW91/6-31+G*), 92 (B3LYP/6-31+G*), and 80 cm^{-1} (local DFT: SVWN5/6-31G**). As shown in Figure 3c, the semiempirical PM3 result also shows rather large (280 cm^{-1}) error. These results indicate that the PW91PW91/6-31+G* and BP86/6-31G* methods are reliable for describing the vibrational properties of CAB and that the dependence of the vibrational frequencies of the N═N modes on the DFT exchange-correlation functional is remarkable. It is expected that the MP2 method with the 6-31+G* basis set is more accurate. However, such a high-level calculation is often formidable for such medium-sized molecules as azobenzene. Therefore, we concluded that the accurate DFT method with a large basis set is practically the most efficient for the analysis of vibrational properties of *trans*- and *cis*-azobenzenes.

4. Conclusions

To clarify the structural and vibrational properties of *trans*-azobenzene (TAB) and *cis*-azobenzene (CAB), molecular orbital calculations based on the HF, MP2, and DFT methods were carried out using four types of basis sets: 6-31G*, 6-31G**, 6-311G**, and 6-31+G*. The most striking finding in the present study is that the MP2 calculation utilizing the diffuse basis set (6-31+G*) leads to a distorted structure of TAB, in which the phenyl rings are rotated by 18.5° with respect to the N═N−C plane. This structure is comparable to that obtained by gas-phase electron diffraction experiments.[5] On the other hand, the HF and DFT (PW91PW91, MPW91, BP86, and B3LYP) calculations result in almost planar structures for TAB. These results indicate that the correction for the electron correlation energy by MP2, as well as the 6-31+G* basis set, is necessary to appropriately describe the interaction between the two phenyl rings in TAB. The stable structure of CAB and the relative stability between TAB and CAB are described by the DFT and MP2 methods with reasonable accuracy.

For the optimized structures of TAB and CAB, the vibrational frequencies and its corresponding eigenvectors were calculated. Because the analysis with the MP2/6-31+G* was impossible due to the limitations of computational resources, the 6-31G* basis set was used for the MP2 analysis. The MP2 results for TAB and CAB show rather large errors (170 and 70 cm^{-1}) in frequency compared with experiment, indicating that this MP2 analysis is insufficient for predicting the vibrational frequencies. On the other hand, the PW91PW91/6-31+G* and BP86/6-31G* methods provide vibrational frequencies comparable to experiment, of which the errors in frequency are at most 26 and 32 cm^{-1}, respectively. Therefore, we concluded that the accurate DFT method with a large basis set is efficient for the analysis of vibrational properties for azobenzene. We expect that the present study will provide useful benchmark data on the accuracy of MP2 and DFT methods for describing the structural and vibrational properties of those aromatic molecules similar to azobenzene.

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