

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/244134424>

Ab initio study of the torsional potential for 9-phenylanthracene in the ground and excited states

ARTICLE *in* CHEMICAL PHYSICS LETTERS · MARCH 2003

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(03)00216-1

CITATIONS

12

READS

18

2 AUTHORS, INCLUDING:



Ken Sakata

Hoshi University

37 PUBLICATIONS 473 CITATIONS

SEE PROFILE

Ab initio study of the torsional potential for 9-phenylanthracene in the ground and excited states

Ken Sakata ^{a,*}, Kimihiko Hara ^b

^a School of Pharmacy and Pharmaceutical Sciences, Hoshi University, Shinagawa-ku, Tokyo 142-8501, Japan

^b Research Center for Low Temperature and Materials Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

Received 14 November 2002; in final form 27 January 2003

Abstract

Torsional potentials of 9-phenylanthracene both in the ground and excited states were determined by using ab initio molecular orbital calculations. Molecular structure in the ground state was optimized at the restricted Hartree–Fock level under the C_{2v} symmetry. Then, the torsional potentials between the anthracene ring and the phenyl group in the S_0 and S_1 states were calculated by means of multi-reference perturbation theory based on the complete active space (CAS) SCF wave function. The present findings were consistent with the jet-laser experimental results by Barbara et al.

© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

Torsional motion in a molecule plays an important role in the study of chemical reactions and kinetics [1–6]. Quantum chemical calculation of the torsional potential is utilized not only for the determination of the conformational structure [7–11], but also it is useful for understanding the chemical kinetics of isomerization reactions [12]. Recent progress of laser experimental techniques enables us to obtain the precise experimental data for the torsional motion. For example, Barbara and co-workers [13–15] investigated the vibrational structures of substituted anthracene deriv-

atives by laser-induced fluorescence (LIF) and determined the torsional potential of the bond connecting the anthracene ring and various substituents. On the other hand, estimation of the torsional potential function by quantum chemical calculations is also a powerful tool since it provides the data of isolated molecule without influence of solvent or other solute molecule. In spite of the progress in quantum chemistry, the accurate description of both ground and excited electronic states in large molecules remains an important problem, especially for the molecules having more than 10 non-hydrogen atoms [16].

In the present study, we have investigated the torsional potentials of the ground (S_0) and excited (S_1) states for 9-phenylanthracene (9PA) by using ab initio molecular orbital (MO) calculations. As far as we know, there is no study of 9PA by using

* Corresponding author. Fax: +81-3-3787-0429.
E-mail address: sakata@hoshi.ac.jp (K. Sakata).

ab initio calculations. 9PA having 20 carbon atoms and 14 hydrogen atoms with high symmetry, as shown in Fig. 1, is almost the maximum size to obtain accurate results by the ground- as well as excited states MO calculations. Whereas, it is such a large enough molecule that reliable experimental data are available. Barbara and co-workers [13] have observed the free-jet LIF spectra of 9PA and obtained the best-fit potentials of both S_0 and S_1 states by fitting the torsional energy levels to a simple potential. Theoretically, Gustav [17] has performed the calculations of 9PA using the hybrid method of the empirical and semi-empirical methods proposed by Warshel and Karplus [18], in which equilibrium geometries of 9PA in the electronic states of S_0 , S_1 , and T_1 have been investigated and these electronic spectral properties have been compared with absorption and fluorescence observations. Wortmann et al. [19] have studied the optical fluorescence spectra of 9,9'-bianthryl (99BA) and 9PA in 2-methylbutane (2MB) and in 2MB/benzene mixed solvents. They have also investigated the ground-state potential by semi-empirical AM1 method. However, these theoretical studies were carried out by using empirical and semi-empirical methods. The more accurate calculations are needed in order to obtain the reliable results for comparing with experimental observations. It is known that the semi-empirical method often fails even to give a qualitatively correct potential for the rotation about single bonds in conjugated molecules [8,11]. In this Letter, we report the torsional potentials

between the anthracene ring and the phenyl group in the S_0 and S_1 states, which were calculated by the multi-reference perturbation theory based on the complete active space (CAS) SCF wave function. We attempted to compare them with the potentials determined by Barbara and co-workers [13].

2. Computational procedure

The stable structure in the ground state of 9PA was optimized within the C_{2v} symmetry ($\phi = 90^\circ$) by using the restricted Hartree–Fock (RHF) method. The theoretical harmonic vibrational frequencies were obtained from the analytical second derivatives to verify the equilibrium structure as a true minimum. Then the single-excitation configuration interaction (SCI) calculations were performed in order to estimate the electronic character in the excited states. In the SCI calculations, the lower molecular orbitals corresponding to the inner-shells were treated as frozen orbitals. For these calculations, Dunning–Hay’s (9s5p/4s)/[3s2p/2s] contracted basis set (DZV) [20] was employed for the Gaussian basis functions.

Next, the torsional potential energies of both S_0 and S_1 states were calculated using the geometries which were optimized with each torsional angle ϕ (50° – 130°) under the C_2 symmetry at the RHF/DZV level of theory. Here, the torsional angle ϕ was defined by the dihedral angle $C_{2'}-C_{1'}-C_9-C_a$. On the basis of the results in the SCI calculations, we regarded the four orbitals ($4a_2$, $11b_2$, $12b_2$, and $5a_2$) as active orbitals for the CASSCF calculations. That is, 4-in-4 CASSCF wave functions were obtained for both S_0 and S_1 states. By applying these CASSCF wave functions to the reference configurations, we carried out the calculations of second-order perturbation method based on the multi-configuration quasi-degenerate perturbation theory (MCQDPT) [21,22]. In the present study we used the single-state perturbation calculations, so the method is the same as multi-reference Møller–Plesset perturbation theory [23,24]. For the CASSCF/MCQDPT calculations, the DZV plus d-type polarization function ($\alpha = 0.75$) to C atoms

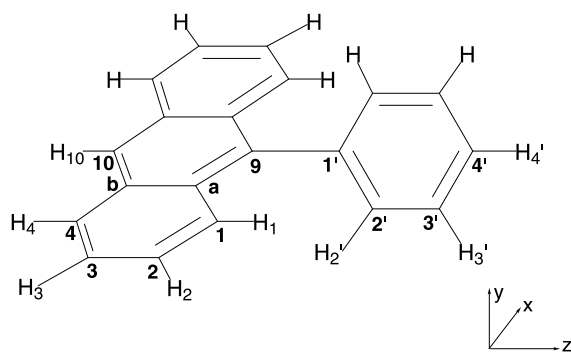


Fig. 1. Atom numbering of 9-phenylanthracene (9PA).

was used for the basis set. The MO calculations were performed by GAMESS program package [25].

3. Results and discussion

3.1. Stable structure in the ground state

The optimized geometrical parameters thus obtained are listed in Table 1. The atom numbering is represented in Fig. 1. The bond length linking between anthracene and phenyl group, $r(\text{C}_{1'}\text{C}_9)$, is 1.501 Å. This bond length is slightly longer than the bond lengths linking between anthracene and alkenyl group of 2-vinyanthracene (2VA) as well as 2-(2' propenyl)anthracene (22PA), which have been calculated at the same level of theory in our previous study (1.479 Å in *s-trans* form of 2VA and 1.495 Å in *s-trans* form of 22PA) [12]. The harmonic vibrational frequencies are given in Table 2. All the frequencies have real numbers, so that the C_{2v} structure ($\phi = 90^\circ$) is a true minimum at the RHF/DZV level of theory. It was also confirmed that the lowest vibrational frequency, 34 cm^{-1} , corresponds to the torsional vibration between anthracene and phenyl group.

Next, we performed the SCI calculations in order to estimate the electronic character of the excited states. The orbital energy diagram near the HOMO and LUMO is illustrated in Fig. 2. The excitation energies, oscillator strengths, and the main configuration state functions (CSFs) are given in Table 3. In the first excited state, S_1 , the wave function has A_1 symmetry and the excitation energy is 4.39 eV. The main CSFs which consist of the wave function are $\text{HOMO}(11b_2) \rightarrow \text{LUMO}(12b_2)$, $(\text{HO} - 1)\text{MO}(4a_2) \rightarrow (\text{LU} + 1)\text{MO}(5a_2)$, and $(\text{HO} - 1)\text{MO}(4a_2) \rightarrow (\text{LU} + 3)\text{MO}(6a_2)$. These CI coefficients are 0.924, -0.274 , and -0.135 , respectively. As shown in Fig. 2, these MOs consist of the π orbitals of anthracene and phenyl group, and the amplitudes of these MOs are larger in anthracene part. On the other hand, the wave function in the second and third excited states, (S_2 and S_3), have B_1 symmetry and their excitation energies are 4.89 and 6.01 eV, respectively. As a result, we re-

Table 1

Optimized geometrical parameters of 9PA at the RHF/DZV level

Bond distances ^a	
$r(\text{C}_{1'}\text{C}_9)$	1.501
$r(\text{C}_9\text{C}_a)$	1.408
$r(\text{C}_a\text{C}_b)$	1.433
$r(\text{C}_{10}\text{C}_b)$	1.393
$r(\text{C}_a\text{C}_1)$	1.443
$r(\text{C}_1\text{C}_2)$	1.360
$r(\text{C}_2\text{C}_3)$	1.436
$r(\text{C}_3\text{C}_4)$	1.358
$r(\text{C}_b\text{C}_4)$	1.440
$r(\text{C}_{1'}\text{C}_{2'})$	1.399
$r(\text{C}_{2'}\text{C}_{3'})$	1.395
$r(\text{C}_{3'}\text{C}_{4'})$	1.395
$r(\text{C}_1\text{H}_1)$	1.069
$r(\text{C}_2\text{H}_2)$	1.072
$r(\text{C}_3\text{H}_3)$	1.071
$r(\text{C}_4\text{H}_4)$	1.072
$r(\text{C}_{10}\text{H}_{10})$	1.073
$r(\text{C}_{2'}\text{H}_{2'})$	1.072
$r(\text{C}_{3'}\text{H}_{3'})$	1.072
$r(\text{C}_{4'}\text{H}_{4'})$	1.071
Bond angles ^b	
$\angle(\text{C}_{1'}\text{C}_9\text{C}_a)$	119.9
$\angle(\text{C}_9\text{C}_a\text{C}_b)$	119.7
$\angle(\text{C}_9\text{C}_a\text{C}_1)$	122.5
$\angle(\text{C}_a\text{C}_b\text{C}_{10})$	119.5
$\angle(\text{C}_a\text{C}_b\text{C}_4)$	119.2
$\angle(\text{C}_a\text{C}_1\text{C}_2)$	121.2
$\angle(\text{C}_1\text{C}_2\text{C}_3)$	120.7
$\angle(\text{C}_2\text{C}_3\text{C}_4)$	120.0
$\angle(\text{C}_3\text{C}_4\text{C}_b)$	121.1
$\angle(\text{C}_9\text{C}_{1'}\text{C}_{2'})$	120.6
$\angle(\text{C}_{1'}\text{C}_{2'}\text{C}_{3'})$	120.7
$\angle(\text{C}_{2'}\text{C}_{3'}\text{C}_{4'})$	120.2
$\angle(\text{H}_1\text{C}_1\text{C}_a)$	118.9
$\angle(\text{H}_2\text{C}_2\text{C}_1)$	120.1
$\angle(\text{H}_3\text{C}_3\text{C}_2)$	119.4
$\angle(\text{H}_4\text{C}_4\text{C}_3)$	120.6
$\angle(\text{H}_{10}\text{C}_{10}\text{C}_b)$	119.3
$\angle(\text{H}_{2'}\text{C}_{2'}\text{C}_{1'})$	119.4
$\angle(\text{H}_{3'}\text{C}_{3'}\text{C}_{2'})$	119.8
$\angle(\text{H}_{4'}\text{C}_{4'}\text{C}_{3'})$	120.2
Dihedral angle ^b	
$\phi(\text{C}_{2'}\text{C}_{1'}\text{C}_9\text{C}_a)$	90

^a Bond distances are given by Å.

^b Angles are given by degree.

gard the eigenstate, which has the A_1 symmetry, as the S_1 state in the calculations of the torsional potential.

Table 2
Vibrational frequencies at the RHF/DZV level

Harmonic vibrational frequencies (cm ⁻¹)
34(a ₂), 73(b ₂), 74(b ₁), 101(b ₂), 134(a ₂), 212(a ₁), 242(b ₂), 261(a ₂), 281(b ₁), 344(a ₁), 373(b ₂), 426(a ₁), 453(b ₁), 459(a ₂), 478(b ₂), 542(a ₂), 555(b ₁), 564(a ₂), 634(b ₂), 642(b ₁), 679(b ₁), 684(b ₂), 691(a ₁), 707(a ₁), 732(b ₂), 754(a ₁), 802(b ₁), 852(a ₂), 858(b ₂), 861(b ₁), 881(a ₂), 908(a ₁), 919(b ₁), 929(b ₂), 990(a ₂), 992(b ₂), 996(a ₂), 1020(b ₁), 1028(a ₁), 1067(b ₂), 1075(b ₁), 1095(a ₁), 1097(a ₁), 1106(b ₁), 1132(a ₂), 1133(a ₁), 1137(b ₂), 1141(a ₂), 1152(a ₂), 1152(b ₂), 1159(b ₁), 1188(b ₂), 1203(b ₁), 1227(b ₁), 1265(a ₁), 1273(b ₂), 1313(a ₁), 1321(b ₁), 1321(a ₁), 1324(a ₁), 1356(b ₂), 1358(b ₁), 1395(a ₁), 1430(b ₁), 1436(a ₁), 1483(b ₂), 1500(a ₁), 1542(b ₁), 1552(b ₁), 1582(a ₁), 1596(b ₂), 1607(a ₁), 1610(b ₁), 1643(a ₁), 1663(a ₁), 1700(b ₁), 1760(a ₁), 1763(b ₂), 1763(b ₁), 1799(a ₁), 1828(a ₁), 1833(b ₁), 3382(a ₁), 3387(b ₁), 3388(a ₁), 3389(a ₁), 3395(b ₂), 3400(b ₁), 3400(a ₁), 3406(a ₁), 3415(b ₂), 3418(b ₁), 3419(a ₁), 3427(a ₁), 3439(b ₁), 3440(a ₁)

3.2. Torsional potentials in the ground and excited states

When the torsional motion is investigated by the analysis of the vibrational spectrum, the torsional angle has generally been chosen as the coordinate instead of the normal coordinate [3,13–15]. As mentioned above, we confirmed that the lowest vibrational mode in the S₀ state corresponds to the torsional motion at the RHF level of theory. Based on the result, the torsional potential and the following vibrational levels have been examined at the higher level of theory under the assumption that the normal mode of the torsional motion can be approximated to the torsional angle in both the S₀ and S₁ states.

Using the geometries optimized with each torsional angle, ϕ , at the RHF/DZV level of theory, the torsional potentials were calculated. The cal-

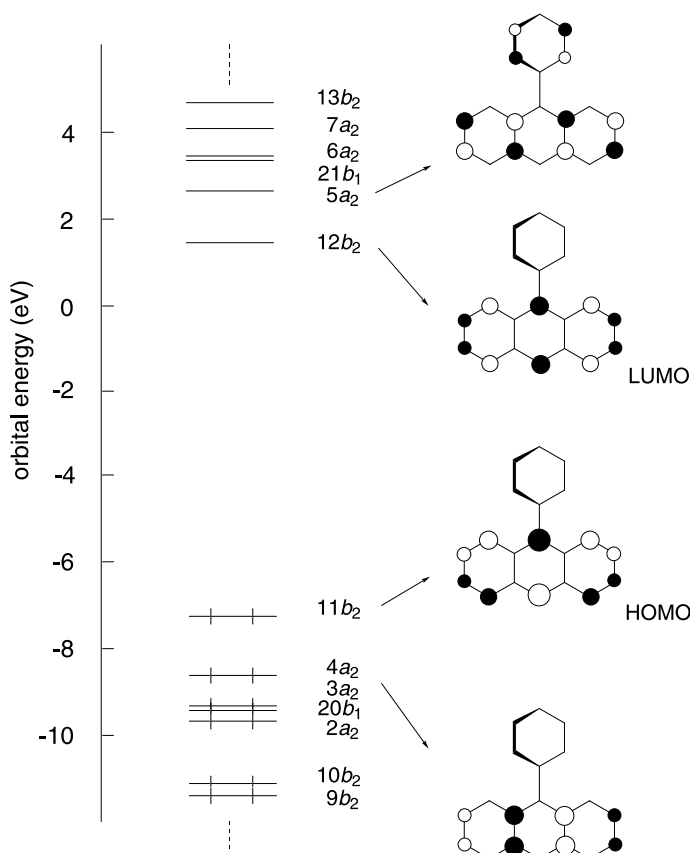


Fig. 2. Orbital energy diagram of 9PA at the C_{2v} geometry.

Table 3

Excitation energies, oscillator strengths, and the main configuration state functions (CSFs) of 9PA by means of the SCI method

	Excitation energy (eV)	Oscillator strength	Main CSFs ^a
S ₁ (A ₁)	4.39	0.289	0.924Φ(11b ₂ → 12b ₂) − 0.274Φ(4a ₂ → 5a ₂) − 0.135Φ(4a ₂ → 6a ₂)
S ₂ (B ₁)	4.89	0.000	0.680Φ(4a ₂ → 12b ₂) + 0.635Φ(11b ₂ → 5a ₂) + 0.276Φ(11b ₂ → 6a ₂) + 0.102Φ(9b ₂ → 7a ₂)
S ₃ (B ₁)	6.01	0.005	0.508Φ(2a ₂ → 12b ₂) − 0.507Φ(11b ₂ → 7a ₂) + 0.448Φ(11b ₂ → 6a ₂) + 0.417Φ(3a ₂ → 12b ₂) − 0.163Φ(11b ₂ → 5a ₂) + 0.141Φ(9b ₂ → 5a ₂) − 0.127Φ(4a ₂ → 14b ₂)

^a The CSFs of which absolute values of CI coefficients are greater than 0.1 are listed.

culated energy data were reproduced by the six-term truncated Fourier expansion:

$$V(\phi) = \frac{1}{2} \sum_{n=1}^6 V_n (1 - \cos n\phi), \quad (1)$$

where $V(\phi)$ is the relative energy at the torsional angle ϕ . In the fitting, the constant parameter was also included in the potential in order to define the point of $\phi = 90^\circ$ as an origin. Because of the symmetry referred to the $\phi = 90^\circ$ plane in the potential, the three terms of V_2 , V_4 , and V_6 in the expansion are necessary. The potential parameters obtained by fitting the calculated energy data to Eq. (1) are given in Table 4. Figs. 3a and b display the potentials of S₁ and S₀ states, respectively. In Fig. 3, the potentials estimated from the LIF spectrum [13] are also represented in broken lines. At $\phi = 90^\circ$, the excitation energy is calculated to be 26 169 cm^{−1} (3.24 eV).

For the torsional potential in the S₀ state, the single-well form which has the minimum at $\phi = 90^\circ$ was obtained, as shown in Fig. 3b. The torsional

potential which we calculated to obtain the geometries with each torsional angle was also represented in Fig. 3b. In the torsional potential at the RHF/DZV level, the curvature at the minimum point $\phi = 90^\circ$ is large and the potential form looks like a harmonic oscillator. On the other hand, torsional potential calculated by the multi-reference perturbation theory is relatively flat near the minimum. Because these potentials were calculated using the same geometries, it is considered that the electron-correlation effect gives this difference. The experimental fitting by Barbara and co-workers [13] shows that ϕ_{\min} is 83° but the barrier in the $\phi = 90^\circ$, ΔV , is 1 cm^{−1}, which is so small. The potential obtained by them is also flat near the $\phi = 90^\circ$. As a result, the ground-state torsional potential which we calculated in this study reproduced the experimental result.

On the other hand, the double-well potential was obtained in the S₁ state. In our preliminary calculations, the double-well potential was not reproduced by the SCI or 4-in-4 CASSCF calculations. As a result, we find that the electron-cor-

Table 4

Potential parameters for S₀ and S₁ states of 9PA (cm^{−1})

	V_2	V_4	V_6	V_8	ΔV	ϕ_{\min}
S ₀						
Jet ^a	−3980.0	−1023.0	—	—	1	83°
AM1 ^b	−4262	−1626	−226	−14	20	73°
HF/DZV (<i>this study</i>)	−8485.4	−2426.3	−292.7	—	0	90°
<i>This study</i>	−7153.4	−2274.8	−220.5	—	0	90°
S ₁						
Jet ^a	−2054.9	−1009.2	—	—	243	60°
in 2MB ^b	−680	−420	180	—	330	59°
<i>This study</i>	−3820.8	−2046.4	−203.6	—	379	58°

^a Ref. [13].^b Ref. [19].

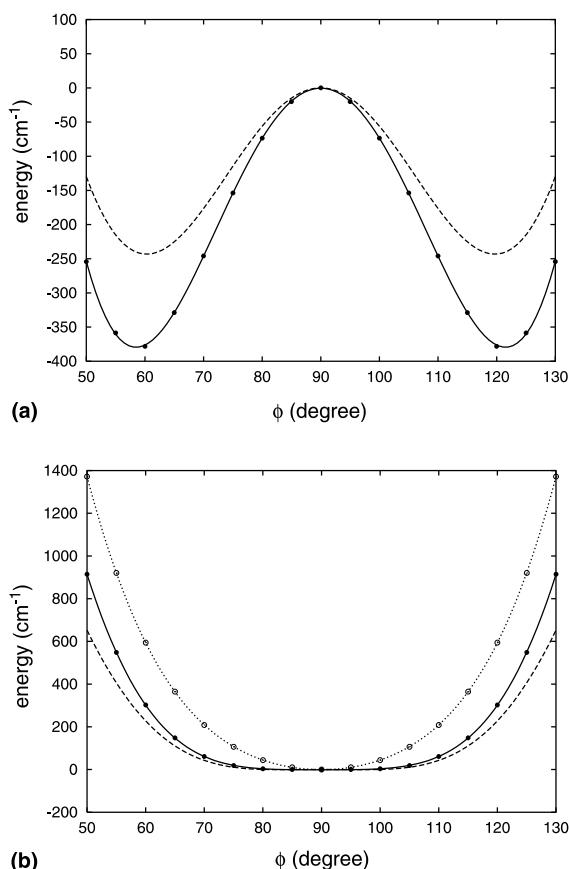


Fig. 3. Torsional potentials of (a) S_1 and (b) S_0 states. The solid lines represent the best fit to Eq. (1). The energy at $\phi = 90^\circ$ is referred to as zero. The potentials obtained by analyzing the LIF spectrum [13–15] are shown in broken lines. The potential at the RHF/DZV level of theory is also shown in dotted line.

relation contribution is also important for the torsional potential in the S_1 state. The same situation has been predicted in the case of 99BA. Kajimoto and co-workers [26] investigated the torsional potential of 99BA by the jet-laser LIF spectrum and concluded that the stable structure in the S_1 state lies at $\phi = 67^\circ$. More recently, Scholes et al. [27] estimated that the torsional angle is 90° in the stable structure by using the SCI calculations. In the case of 99BA, the electron-correlation effect may be necessary in the torsional potential calculations.

By fitting the calculated data to the potential function, the angle where the potential takes a minimum, ϕ_{\min} , was estimated to be 58° , which is in

reasonable agreement with the experimental value of 60° . The result of the calculation by Gustav [17] is 52.5° . The energy barrier, ΔV , is 379 cm^{-1} , which is slightly larger than the experimental value of 243 cm^{-1} . One possible reasoning for the deviation may be the use of the ground-state geometries optimized at the RHF level. It is known that there are small geometrical differences between the S_0 state and the S_1 state in the case of styrene [9] and 2VA [12]. It is considered that in the S_1 state the strain at the $\phi = 90^\circ$ is larger than that near ϕ_{\min} .

3.3. Torsional vibration of phenyl group

Regarding the torsional motion of the phenyl group as expressed by a simple one-dimensional model potential, we calculated the torsional vibrational energy levels by using the potential function $V(\phi)$ obtained above. The one-dimensional Schrödinger equation to be solved is

$$\left(-B \frac{d^2}{d\phi^2} + V(\phi)\right)\psi_n = E_n \psi_n \quad (2)$$

and the rotational constant B is defined as $B = h/8\pi^2 cI$, where I is the reduced moments of inertia, which is represented as

$$I = A \left(1 - \sum_{i=1}^3 \lambda_i^2 \frac{A}{I_i}\right) \quad (3)$$

on the basis of principal axis method [28,29]. Here A is the moment of inertia of the phenyl group, I_i ($i = 1-3$) is the moment of inertia of the whole molecule, and λ_i is the direction cosine between the axis of the phenyl group and the i th principle axis of the whole molecule. Although the geometry is slightly changed concerning the torsional angle ϕ , we assumed that the rotational constant is invariant and then we calculated it based on the C_{2v} optimized structure ($\phi = 90^\circ$). The value of B thus calculated is 0.205 cm^{-1} , which is consistent with the value reported by Barbara and co-workers [13].

For the calculations of eigenvalues and eigenfunctions, we utilized the method developed by Lewis et al. [30]. We used the 70 *cosine* functions as a basis set for calculations. We also calculated using *sine* functions in order to check the calcula-

tions. The results are listed in Table 5. In Table 5, the symmetry designations for each level are also represented. In the designation, the first and second letters (s or a) refer to the 0° and 90° symmetry planes, respectively. The torsional potential obtained by the MO calculations is different from that by experimental analysis, so the torsional vibrational energy levels are necessarily different from the LIF spectrum [13–15]. However, these are qualitatively in agreement with the LIF spectrum data. Moreover, the energy difference between the zero-point energy level in the S_0 state and the zero-point level in the S_1 level is 25815 cm^{-1} , which is in reasonable agreement with the experimental result ($S_0 \rightarrow S_1$ O_0^0 frequency) 26944 cm^{-1} [13–15].

Finally, the Franck–Condon factors between the zero-point energy level in the S_0 state and low-energy levels in the S_1 state were estimated by calculating the square of overlap integral. Because the symmetry of the zero-point level in the S_0 state, a^0 , is ss or as, the energy levels which have the same symmetry becomes non-zero value of overlap integral. In Table 5, the calculated Franck–Condon factors are described as the relative intensity. With increasing the number n of

A^n , the intensity increases from 0.47×10^{-5} for A^0 and it takes a maximum at A^7 . And then it decreases rapidly. The maximum intensity obtained by LIF spectrum is A^4 [13], but the trend in intensity is in qualitative agreement with the experimental results.

4. Concluding remarks

The torsional potentials of 9PA in the ground and excited states have been investigated by using ab initio molecular orbital calculations. The conclusions obtained in the present study are summarized as follows:

(1) On the basis of the ground-state structures optimized at the RHF level, the torsional potentials in both S_0 and S_1 states were estimated using multi-reference perturbation theory. The calculated potential in the S_0 state has a single minimum while the potential in the S_1 state has double minima.

(2) Under the assumption that the torsional motion of phenyl group can be described as a one-dimensional potential, the vibrational energy levels in the S_0 and S_1 states were estimated by using calculated torsional potentials. Moreover, the

Table 5
Torsional vibrational levels (cm^{-1}) in the S_0 and S_1 electronic states

n	E_n	$E_n - E_0$	Symmetry	Assignments	Relative intensity ($a^0 \rightarrow A^n$)
S_0					
0	5.2		ss, as	a^0	
1	20.9	15.7	sa, aa	a^1	
2	41.3	36.1	ss, as	a^2	
3	64.7	59.5	sa, aa	a^3	
4	90.3	85.1	ss, as	a^4	
5	118.0	112.8	sa, aa	a^5	
S_1					
0	−348.7		ss, sa, as, aa	A^0	0.47×10^{-5}
1	−288.4	60.3	ss, sa, as, aa	A^1	0.59×10^{-4}
2	−230.4	118.3	ss, sa, as, aa	A^2	0.37×10^{-3}
3	−174.8	173.9	ss, sa, as, aa	A^3	0.02
4	−122.2	226.5	ss, sa, as, aa	A^4	0.05
5	−73.2	275.5	ss, as	A^5	0.14
6	−73.1	275.6	sa, aa		
7	−30.0	318.7	ss, as	A^6	0.35
8	−28.3	320.4	sa, aa		
9	2.0	350.7	ss, as	A^7	0.38
10	13.7	362.4	sa, aa		
11	36.4	385.1	ss, as	A^8	0.06

Franck–Condon factors between the zero-point energy level in the S_0 state and the low-energy levels in the S_1 state were calculated. The vibrational energy levels in the S_0 state are well consistent with the free-jet LIF spectrum [13]. While the vibrational energy levels in the S_1 state and the peak of the intensity somewhat deviate from the spectrum. This seems to be the fact that the calculated torsional potential is slightly worse. The trend in intensity, however, is consistent with the spectrum.

Acknowledgements

We thank Professor Hiroshi Ichikawa of Hoshi University for valuable discussions.

References

- [1] S.P. Velsko, G.R. Fleming, *J. Chem. Phys.* 76 (1982) 3553.
- [2] J.A. Syage, P.M. Felker, A.H. Zewail, *J. Chem. Phys.* 81 (1984) 4706.
- [3] L.R. Khundkar, A.H. Zewail, *J. Chem. Phys.* 84 (1986) 1302.
- [4] S.R. Flom, V. Nagarajan, P.F. Barbara, *J. Phys. Chem.* 90 (1986) 2085.
- [5] M. Ito, *J. Phys. Chem.* 91 (1987) 517.
- [6] K. Hara, N. Ito, O. Kajimoto, *J. Chem. Phys.* 110 (1999) 1662.
- [7] J. Almlöf, *Chem. Phys.* 6 (1974) 135.
- [8] P. Birner, H.-J. Hofmann, *Int. J. Quantum Chem.* 21 (1982) 833.
- [9] R.J. Hemley, U. Dinur, V. Vaida, M. Karplus, *J. Am. Chem. Soc.* 107 (1985) 836.
- [10] S. Tsuzuki, K. Tanabe, *J. Phys. Chem.* 95 (1991) 139.
- [11] Y. Ni, J.S. Siegel, D.R. Kearns, *J. Phys. Chem.* 95 (1991) 9208.
- [12] K. Sakata, N. Kometani, K. Hara, *Chem. Phys. Lett.* 344 (2001) 185.
- [13] D.W. Werst, W.R. Gentry, P.F. Barbara, *J. Phys. Chem.* 89 (1985) 729.
- [14] D.W. Werst, W.F. Londo, J.L. Smith, P.F. Barbara, *Chem. Phys. Lett.* 118 (1985) 367.
- [15] D.W. Werst, A.M. Brearley, W.R. Gentry, P.F. Barbara, *J. Am. Chem. Soc.* 109 (1987) 32.
- [16] For example B.O. Roos, M. Fülcher, P.-A. Malmqvist, M. Merchán, L. Serrano-Andres, in: S.R. Langhoff (Ed.), *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, Kluwer Academic Publishers, Dordrecht, 1995.
- [17] K. Gustav, *J. Prakt. Chem.* 327 (1985) 291.
- [18] A. Warshel, M. Karplus, *J. Am. Chem. Soc.* 94 (1972) 5612.
- [19] R. Wortmann, S. Lebus, K. Elich, S. Assar, N. Detzer, W. Liptay, *Chem. Phys. Lett.* 198 (1992) 220.
- [20] T.H. Dunning Jr., P.J. Hay, in: H.F. Schaefer III (Ed.), *Methods of Electronic Structure Theory*, Plenum Press, New York, 1977, p. 1.
- [21] H. Nakano, *J. Chem. Phys.* 99 (1993) 7983.
- [22] H. Nakano, *Chem. Phys. Lett.* 207 (1993) 372.
- [23] K. Hirao, *Int. J. Quantum Chem.* S26 (1992) 517.
- [24] K. Hirao, *Chem. Phys. Lett.* 190 (1992) 374.
- [25] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *J. Comput. Chem.* 14 (1993) 1347.
- [26] K. Yamasaki, K. Arita, O. Kajimoto, K. Hara, *Chem. Phys. Lett.* 123 (1986) 277.
- [27] G.D. Scholes, T. Fournier, A.W. Parker, D. Phillips, *J. Chem. Phys.* 111 (1999) 5999.
- [28] B.L. Crawford Jr., *J. Chem. Phys.* 8 (1940) 273.
- [29] C.C. Lin, J.D. Swalen, *Rev. Mod. Phys.* 31 (1959) 841.
- [30] J.D. Lewis, T.B. Malloy Jr., T.H. Chao, J. Laane, *J. Mol. Struct.* 12 (1972) 427.