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Electronic spectra of azaindole and its excited state mixing: A symmetry-adapted cluster configuration interaction study

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Electronic structures of azaindole were studied using symmetry-adapted cluster configuration interaction theory utilizing Dunning's cc-pVTZ basis set augmented with appropriate Rydberg *spd* functions on carbon and nitrogen atoms. The results obtained in the present study show good agreement with the available experimental values. Importantly, and contrary to previous theoretical studies, the excitation energy calculated for the important $n-\pi^*$ state agrees well with the experimental value. A recent study by Pratt and co-workers concluded that significant mixing of $\pi-\pi^*$ and $n-\pi^*$ states leads to major change in the magnitude and direction of the dipole moment of the upper state vibrational level in the $0,0 + 280\text{ cm}^{-1}$ band in the $S_1 \leftarrow S_0$ transition when compared to that of the zero-point level of the S_1 state. The present study, however, shows that all the four lowest lying excited states, ${}^1L_b\ \pi-\pi^*$, ${}^1L_a\ \pi-\pi^*$, $n-\pi^*$, and $\pi-\sigma^*$, cross each other in one way or another, and hence, significant state mixing between them is likely. The upper state vibrational level in the $0,0 + 280\text{ cm}^{-1}$ band in the $S_1 \leftarrow S_0$ transition benefits from this four-state mixing and this can explain the change in magnitude and direction of the dipole moment of the S_1 excited vibrational level. This multistate mixing, and especially the involvement of $\pi-\sigma^*$ state in mixing, could also provide a route for hydrogen atom detachment reactions. The electronic spectra of benzimidazole, a closely related system, were also investigated in the present study. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4935578>]

I. INTRODUCTION

Azaindole [1H-pyrrolo(2,3-b)pyridine] has attracted much attention because its doubly hydrogen bonded dimer undergoes a double proton transfer reaction upon excitation with light. This interesting excited-state double-proton transfer (ESDPT) character of azaindole dimer has led to its use as a model system for DNA base pairs, for which a double proton transfer reaction upon excitation plays an important role in mutations.¹ In early steady-state solution phase experiments, Kasha, El-Bayoumi, and Taylor were the first to demonstrate excited state proton transfer in azaindole.¹ Since then, the photochemistry and photophysics of the azaindole dimer have been extensively studied. In particular, the question of whether proton transfer in the 7-azaindole dimer follows a concerted or a stepwise mechanism has been debated comprehensively (see, for example, Refs. 1–6). Moreover, an analog of tryptophan incorporating the azaindole chromophore has been shown to be useful as an intrinsic protein fluorescence probe.^{7–11} Hence, the excited states of 7-azaindole have attracted much attention in the context of understanding the complex photophysical behavior of tryptophanyl side chains of proteins, especially for the investigations of protein-protein interactions.^{12–19}

In contrast to the dimer, the electronic structure of azaindole has not been as comprehensively studied. Moreover, the existing theoretical results for this molecule are not free from contradictions and show significant deviations from the available experimental results. For example, there is still some doubt about the position of the $n_{\text{pyridine}}-\pi^*$ state (referred to as the $n-\pi^*$ state hereafter), which is likely involved in the all-important photochemistry of this molecule. Using UV/vis spectroscopy in an argon matrix, Ilitch¹² predicted the $n-\pi^*$ state at 4.54 eV, while theoretical studies using complete active space second-order perturbation theory (CAS-PT2) and equation-of-motion coupled cluster with single and double excitation (EOM-CCSD) found the same state at 5.27 and 5.40 eV, respectively.^{15,20} By using jet-cooled spectroscopic study, Kim and Bernstein²¹ suggested a strong vibronic mixing between $L_b\ \pi-\pi^*$ and $n-\pi^*$ states. However, through similar experimental studies, Huang *et al.*¹³ concluded that $S_1\ \pi-\pi^*$ (L_b) state undergoes mixing with the $L_a\ (\pi-\pi^*)$ state and not with the $n-\pi^*$ state. In fact, it has been shown in a recent combined experimental and theoretical study that the $n-\pi^*$ state is mixing with the $\pi-\pi^*$ (L_b) state.²⁰ Furthermore, the other valence excited and Rydberg states, especially $\pi-\sigma_{\text{N-H}}^*$ (hereafter referred to as the $\pi-\sigma^*$ state), which are supposed to be involved in the photochemistry of these types of molecules,^{22,23} do not appear to have been studied before. The $\pi-\sigma^*$ state, which is highly mixed with $\pi-3s$ Rydberg state and lies close in energy to the low-lying $\pi-\pi^*$ states, plays a crucial role in both spectroscopic and photophysical properties of indole and in many aromatic biomolecules,^{22,23}

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and hence, studying this π - σ^* state along with the low-lying Rydberg states in azaindole is important.

Although the electronic spectra of azaindole have been studied experimentally, the π - π^* (L_a) state has not been clearly observed in most of these studies.^{12,19,24,25} A band at 4.49 eV in the magnetic circular dichroism spectrum of azaindole in ethanol was assigned to this state;²⁶ yet, this peak is absent in argon matrix and jet spectra.^{12,25} In contrast, various theoretical studies have identified both the low-lying π - π^* states (1L_b and 1L_a). Shukla and Mishra studied the low-lying valence excited states by using configuration interaction involving singly (CIS) excited configurations.¹⁴ The absorption and emission spectra have been studied by Borin and Serrano-Andres by using the CAS self-consistent field (SCF) method and multi-configurational CAS-PT2.^{15,16} The geometrical changes of the azaindole monomer were investigated by using rotationally resolved electronic spectroscopy as well as a Frank-Condon analysis.^{17,18} In these studies, the nature of the lowest excited state has been shown to be of L_b character. Svartsov and Schmitt studied the lowest electronic excited states (L_b and L_a π - π^* states) of azaindole and azaindole-(H₂O)_{1,2} clusters using time-dependent density functional theory (TD-DFT), coupled cluster singles and doubles model (CC2) by employing the resolution-of-the-identity (RI) approximation, and combined DFT/multireference configuration interaction (DFT/MRCI) methods.²⁷ The CC2 and DFT/MRCI calculations concluded that the first excited state is L_b π - π^* state, but the TD-DFT (with B3LYP functional) reverses the order by making L_a as the first excited state. Indeed, in an earlier study, we showed that the use of TD-DFT in conjunction with several different density functionals failed to predict the correct order of these two low-lying π - π^* states in indole and azaindole.²⁸

Recently, Pratt and co-workers²⁰ combined high-resolution electronic spectroscopy and EOM-CCSD and showed that the dipole moment of the upper state vibrational level in the 0,0 + 280 cm⁻¹ band in the $S_1 \leftarrow S_0$ transition is twice as large as that of the zero-point level of the S_1 state. They made the important observation that the lowest lying π - π^* and n - π^* states cross one another and as this vibrationally excited S_1 π - π^* state is energetically close to the S_3 n - π^* minimum, significant state mixing is possible, which leads to the major change in the magnitude and direction of the dipole moment of the excited vibrational level. Given this interesting study, we wondered if the mixing of the other states, L_a π - π^* and π - σ^* , with the first π - π^* state, may also be possible. This is because (1) the dipole moment of the upper state vibrational level is substantially larger (4.6 D) than that of zero-point level of the S_1 and S_3 states (around 2 D), (2) the closely lying charge-transfer-like L_a π - π^* state is supposed to have a large dipole moment, and (3) mixing of π - σ^* state with the low-lying π - π^* states is evident in similar aromatic biomolecules.^{22,23} This leads us to postulate that the mixing of these L_a π - π^* and π - σ^* states, that are expected to be highly polar, with the L_b π - π^* state might have also contributed to the change in magnitude and direction of the dipole moment of the upper state vibrational level in the 0,0 + 280 cm⁻¹ band.

The character of the excited state can be revealed by the orientation of its electronic transition dipole moment

(TDM), which is the dipole moment of the oscillating charge density and a measure of the charge that is shifted during the excitation. For a $S_0 \rightarrow S_1$ excitation, it is defined as $\langle \mu_{TDM} \rangle = \int \psi_{S_1}^* \mu \psi_{S_0} d\tau_e$, where ψ_{S_1} and ψ_{S_0} are the wave functions of the corresponding states S_1 and S_0 , μ is the electronic dipole operator, and the integral runs over the coordinates of all electrons. The transition dipole moment of the lowest π - π^* state has been determined theoretically as well as experimentally. Earlier, semi-empirical studies predicted this value as +7.5° or -0.8° with the long molecular axis.^{12,29} From a CASSCF study, Borin and Serrano-Andres obtained a value of +27°.¹⁵ The predicted value using DFT/MRCI theory is +20.5°.²⁷ The evaluation of a rotational contour by Hassan and Hollas²⁴ resulted in an angle $\pm 15^\circ$. Nakajima *et al.*³⁰ obtained a value of $\pm 21^\circ$ from a rotational resolved LIF spectrum. In these two experimental studies, only the square of the transition dipole moment has been obtained, leaving the sign undetermined. Recently, using the rotationally resolved laser-induced fluorescence spectroscopy, Schmitt *et al.*¹⁸ and Kang *et al.*¹⁹ found this value as -21° and -14.2°, respectively. A recent experimental study confirmed the negativity of this quantity.³¹ All these recent experimental observations are in contrast to the findings of most of the theoretical studies, which predict a positive angle.

Considering the importance of the photochemistry of this molecule, accurate knowledge on its electronic structure is vital. Thus, in the present work, we use symmetry-adapted cluster³²-configuration interaction³³⁻³⁵ (SAC-CI) theory to obtain the electronic spectra of azaindole and to assign its valence as well as its Rydberg transitions, including both singlet and triplet excitations. In this way, we hope to ascertain the extent to which mixing of the various excited states with the first π - π^* state contributes to its behavior, and in this way reconcile theory with experiment. We believe that resolving these fundamental issues shed more light on the photochemistry of this important molecule.

II. COMPUTATIONAL DETAILS

All computations were performed with the GAUSSIAN09 suite of programs.^{36,37} In addition to the title azaindole molecule, benzimidazole, a closely related molecule, is also considered for the present investigation. The ground-state structures were first optimized and confirmed to be minima via frequency calculations by using B3LYP functional^{38,39} with 6-311+G(*d,p*) basis set. Second, the structures were optimized at CCSD theory⁴⁰⁻⁴² with 6-311+G(*d,p*) basis set [Cartesian coordinates in the supplementary material (Ref. 43)]. The vertical absorption spectra were then obtained using the SAC-CI singles and doubles (SD)-*R* method with LevelThree accuracy utilizing Dunning's valence triple-zeta basis set, cc-pVTZ, for carbon and nitrogen atoms, and Dunning's valence double-zeta basis set, cc-pVDZ, for hydrogen atoms at the CCSD optimized structures.⁴⁴ These basis sets were duly augmented with two sets of Rydberg *spd* functions for carbon ($\zeta_s = 0.0437$ and 0.017 25, $\zeta_p = 0.0399$ and 0.015 75, $\zeta_d = 0.0285$ and 0.011 25) and two sets for nitrogen ($\zeta_s = 0.0532$ and 0.021, $\zeta_p = 0.0475$ and 0.018 75, $\zeta_d = 0.0285$ and 0.011 25) atoms. In both the cases, the

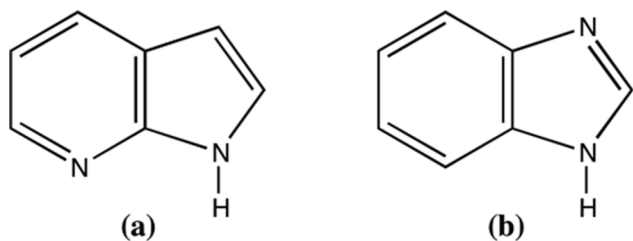


FIG. 1. Schematic structures of (a) azaindole and (b) benzimidazole.

electronic spectra calculations include low-lying fourteen, seven in each symmetry groups, A' and A'' , singlet excited states (both valence as well as Rydberg $3s$, $3p$, and $3d$ states). For convenience, we refer “ σ ” and “ π ” to denote in-plane and out-of-plane Rydberg orbitals, respectively. The six low-lying triplet excited states were also studied. Electronic spectra calculations were performed within C_s symmetry, with the molecule placed in the xy plane. Apart from the excitation energies, we have also calculated the dipole moments of all the studied excited states due to their biological relevance.

III. RESULTS AND DISCUSSION

Both azaindole and benzimidazole have C_s symmetry and because of the symmetry, theoretically all the transitions are optically allowed. The schematic structures of azaindole and benzimidazole are given in Figure 1.

A. TD-DFT benchmarking

Before moving to the main subject, let us discuss briefly the TD-DFT results on azaindole. In an earlier study,²⁸ we concluded that most of the density functionals tested were unable to foretell the right order of the two low-lying L_b and L_a π - π^* states of indole and azaindole molecules. Although we have tested wide variety of density functionals in that study, the performance of double-hybrid (DH) functionals was not examined. In recent years, DH functionals, which uses the combination of correlation energy arising from PT2

together with a correlation energy functional in addition to the hybrid combination of Hartree-Fock exchange energy and an exchange energy functional,^{45–47} have shown to provide accurate excitation energies even for problematic systems.^{48–52} To check the performance of DH functionals for this important molecule, we studied its four low-lying singlet states using B2PLYP (Ref. 45) and mPW2PLYP.⁴⁶ The same basis set, the 6-311+G(2d,p) augmented with two sets of Rydberg sp functions for carbon and nitrogen, that was used for the earlier TD-DFT calculations²⁸ was also utilized here. The obtained results are given in Table I along with the available experimental values.

Table I shows that both the double-hybrid functionals, B2PLYP and mPW2PLYP, wrongly predict that the 1L_a state is the lowest excited state in azaindole, as concluded by most of the density functionals tested previously,²⁸ and the 1L_b state lies 0.13 eV above the 1L_a state. Also, both the DH functionals overestimate the 1L_b state by 0.8 eV. Though the charge transfer-like nature of the 1L_a state can explain the failure of the TD-DFT calculations in determining the order of these two states, overestimating the 1L_b π - π^* state by 0.8 eV is a big concern. In fact, DFT predicts similar dipole moments for both these π - π^* states when in fact the 1L_a state is expected to have a larger dipole moment (see the SAC-CI results). Another issue is the position of the n - π^* state. A recent high-level *ab initio* study²⁰ concluded that the lowest lying A'' state is the n - π^* state (see also the SAC-CI results in Sec. III B). However, both of the DH functionals calculated this n - π^* state as the 2nd lowest state in the A'' symmetry, next to the π - $3s$ and π - σ^* state. The calculated excitation energies for this n - π^* state are 1.1 eV higher than the value observed in an experimental study¹² (see Table I). It should be noticed here that unlike these DH functionals, all the hybrid, meta-GGA, and long-range corrected functionals used in the earlier study²⁸ correctly identified that this n - π^* state is the lowest state in the A'' symmetry. So DH functionals are not only unable to predict the right order of the two low-lying π - π^* states in azaindole, but they also overestimate its 1L_b π - π^* and n - π^* states by more than 0.8 and 1.1 eV, respectively.

There are a few possible ways to improve the quality of the computational methodology utilized in the present

TABLE I. Calculated vertical excitation energies (ΔE in eV), oscillator strengths (f), and dipole moments (μ in D) for the low-lying four singlet excited states of azaindole.^a

Method	π - π^* 1L_b state			π - π^* 1L_a state			n - π^*			π - $3s$ and π - σ^* ($N-H$)		
	ΔE	f	μ	ΔE	f	μ	ΔE	f	μ	ΔE	f	μ
B2PLYP	5.09	0.042	2.96	4.96	0.187	3.84	5.66	0.003	1.91	5.35	0.008	9.41
mPW2PLYP	5.10	0.039	3.04	4.97	0.193	3.69	5.69	0.002	2.01	5.28	0.008	8.56
B2PLYP ^b	5.13	0.044	2.69	4.97	0.190	3.91	5.61	0.003	1.92	5.35	0.008	8.75
Expt. ^c	4.28, 4.29 ^{d-f}			2.30 ^g			4.56			<0.01		

^aTD-DFT using the 6-311+G(2d,p) basis set augmented with two sets of Rydberg diffuse functions [2s,2p] on C and N atoms at the CCSD/6-311+G(d,p) optimized structure.

^bBoth ground-state optimization and vertical TD-DFT calculation using the B2PLYP functional with 6-311++ G(3df,3pd) basis set augmented with two sets of Rydberg diffuse functions [2s,2p] on C and N atoms.

^cReference 12.

^dReference 24.

^eReference 25.

^fReference 19.

^gReference 54.

^hReference 26.

TD-DFT study: (1) by increasing the size of the basis set and (2) by using the same theory (both functional and the basis set) for both ground-state optimization and vertical excited state energy calculation. The latter approach could at least offer more consistency in the calculation. The basis set we used, 6-311+G(2*d*,*p*), has been shown to be adequate for the TD-DFT calculations of low-lying vertical excited states of large set of molecules.⁵³ Also, the 6-311+G(2*d*,*p*) basis set is duly added with two sets of Rydberg *sp* functions for carbon and nitrogen atoms for the present calculations and so, the basis set used in the present study should be sufficient enough for the TD-DFT calculation. Nonetheless, a larger basis set could be used. The second factor is the ground state geometry. For the consistency with our earlier study,²⁸ we used CCSD/6-311+G(*d*,*p*) optimized structure for the vertical excited state calculations. Nevertheless, to meet the second criteria as well as the first, we re-performed the calculations using same theory for both the ground-state optimization and the vertical excitation energy calculations (i.e., using B2PLYP DH functional with a larger 6-311++G(3*df*,3*pd*) basis set augmented with two sets of Rydberg *sp* functions for carbon and nitrogen atoms). The results are also given in Table I. As seen from the table, the results are not significantly different from the earlier ones, a maximum improvement of 0.05 eV is noticed for the *n*- π^* state. So it is clear that the TD-DFT problem with the azaindole molecule remains unsolved, even using the double-hybrid functionals.

B. SAC-CI results

Returning to the SAC-CI calculations, the calculated vertical singlet excitation energies, oscillator strengths, dipole moments, along with the available other theoretical and experimental values are tabulated in Table II. The predicted first excited singlet state in azaindole is $^1L_b \pi-\pi^*$, which agrees with the conclusions made in earlier experimental and high-level theoretical studies. Experimentally, the band origin was established at 4.29 eV in the vapor phase, supersonic jet, and argon matrix spectra.^{12,19,24,25} It has also been argued that this value should be considered as band origin and maxima in the vapor phase.^{24,15} The calculated SAC-CI value is around 0.25 eV smaller than the experimental value. In fact, obtaining very close agreement between theoretical and experimental values for the $\pi-\pi^*$ transitions is not easy, even in ethylenic molecules. By using CAS-PT2 level of theory, Borin and Serrano-Andres¹⁵ calculated this value as 4.22 eV, which is very close to the experimental value; however, a later study by Brause *et al.*¹⁷ by using the same CAS-PT2 theory predicted this value as 4.43 eV. The same state is obtained at 4.52 and 4.82 eV in DFT/MRCI and RICC2 theories, respectively.²⁷ A recent EOM-CCSD study found the excitation energy of this state as 4.85 eV and the adiabatic excitation energy for this state is calculated as 4.67 eV.²⁰ By considering the deviations of all these theoretically calculated values from the experimental one, the value obtained using SAC-CI is reasonable.

TABLE II. Low-lying singlet excited states of azaindole obtained using SAC-CI (LevelThree) with cc-pVTZ basis set for C and N, and cc-pVDZ basis set for H incorporated with Rydberg [2*s*,2*p*,2*d*] diffuse functions on C and N atoms at CCSD/6-311+G(*d*,*p*) optimized geometry. Excitation energies (ΔE), oscillator strengths (*f*), second moments ($\langle r^2 \rangle$), and dipole moments (μ).

State	Nature	SAC-CI				ΔE (eV)	
		ΔE (eV)	<i>f</i>	$\langle r^2 \rangle$	μ (D)	Other theory	Expt.
$1^1A'$	Ground state			978.6	1.57		
$2^1A'$	$\pi-\pi^*$ (L_b)	4.03	0.094	976.8	1.31	4.52, ^a 4.82, ^b 4.22, ^c 4.43, ^d 4.85 ^e	4.28, ^f 4.29 ^{g-i}
$3^1A'$	$\pi-\pi^*$ (L_a)	4.23	0.159	977.6	6.58	4.74, ^a 5.00, ^b 4.49, ^c 4.92, ^d 5.19 ^e	4.49 ^j
$1^1A''$	$n-\pi^*$	4.61	0.005	976.8	2.35	5.27, ^c 5.40 ^e	4.56 ^f
$2^1A''$	$\pi-3s$ and $\pi-\sigma^*$	4.83	0.007	1047.3	7.83		
$3^1A''$	$\pi-3p\sigma$	5.27	0.004	1057.3	2.39		
$4^1A''$	$\pi-3s$ and $\pi-3p\sigma$	5.32	0.002	1056.0	2.97		
$5^1A''$	$\pi-3p\sigma$	5.44	0.003	1077.7	2.09		
$4^1A'$	$\pi-3p\pi$	5.48	0.002	1063.2	1.98		
$6^1A''$	$\pi-3p\sigma$	5.66	0.001	1077.9	0.76		
$5^1A'$	$\pi-3p\pi$	5.81	0.001	1065.3	1.39		
$7^1A''$	$\pi-3d\sigma$	5.87	0.000	1104.2	8.98		
$6^1A'$	$\pi-\pi^*$ and $\pi-3d\pi$	5.93	0.401	1036.5	1.40		
$7^1A'$	$\pi-3d\pi$ and $\pi-\pi^*$	6.01	0.106	1096.9	1.01		
$8^1A'$	$\pi-3d\pi$ and $\pi-\pi^*$	6.15	0.068	1093.8	6.01		

^aDFT/MRCI values taken from Ref. 27.

^bRICC2 values taken from Ref. 27.

^cCAS-PT2 values taken from Ref. 15.

^dCAS-PT2 values taken from Ref. 17.

^eReference 20.

^fReference 12.

^gReference 24.

^hReference 25.

ⁱReference 19.

^jReference 26.

The next state found by the SAC-CI calculation, $\pi-\pi^*$ 1L_a , lies at 4.23 eV. Experimental data for this $\pi-\pi^*$ state are very scarce—only a magnetic circular dichroism study in ethanol found a band at 4.49 eV and it was assigned to this state;²⁶ however, this peak is absent in argon matrix and jet spectra.^{12,25} The CAS-PT2 studies by Borin and Serrano-Andres¹⁵ and Brause *et al.*¹⁷ found this state at 4.49 and 4.92 eV, respectively. The DFT/MRCI and RICC2 values differ from the available experimental value by 0.25 and 0.51 eV, respectively.²⁷ In fact, the recent theoretical study using EOM-CCSD theory overestimates this state by 0.7 eV.²⁰ Given these uncertainties, the SAC-CI calculation is again in reasonable agreement with experiment. The predicted oscillator strengths reveal that 1L_a is more intense than the 1L_b state, as it has been concluded in previous theoretical studies. All of these results point to the strong existence of this bright state and so its absence in most of the available experimental studies is surprising. Moreover, as noted in earlier studies, the dipole moment calculated for the 1L_a state is much higher than that for the 1L_b state, and thus, it should be preferentially stabilized in polar solvent.

In a UV/vis spectroscopic study,¹² Ilich identified the singlet $n-\pi^*$ transition at 4.54 eV with a very weak intensity ($f < 0.01$), and also showed that the $^3(n-\pi^*)$ plays an important role in the phosphorescence emission loss of azaindole. Contrarily, earlier theoretical calculations predicted this $n-\pi^*$ state at a higher energy: at 5.27 eV by CAS-PT2 (Ref. 15) and 5.40 eV by EOM-CCSD,²⁰ giving a deviation from experiment of up to 0.86 eV. In contrast, the present SAC-CI calculations predict 4.61 eV with a very small oscillator strength (0.005), which agrees excellently with the experimental value of Ilich.

We studied the low-lying Rydberg states and the nature of these states can be confirmed by comparing their spatial extensions ($\langle r^2 \rangle$) with that of the ground state. None of the Rydberg states in azaindole were studied earlier though some of them could be involved in the excited-state chemistry of this molecule. As in the case of indole,^{22,23,55} the wave function of the lowest Rydberg state is dominated by the electronic configuration $\pi \rightarrow \sigma^*$, which is the lowest $\pi-\sigma^*$ Rydberg-like state with the σ^* orbital essentially localized on the NH moiety and having a node along the NH bond. We simply refer this state as $\pi-3s$ and $\pi-\sigma^*$ state. The calculated excitation energy for this state in azaindole, 4.83 eV, is very close to that obtained in the indole system, 4.85 eV and 5.05 eV.^{22,55} This indicates that as in the case of indole, this state could also play an important role in the photochemistry of azaindole. All

other low-lying Rydberg states studied in the present study are tabulated in Table II. The $6^1A'$ and $7^1A'$ states, especially the former one, have large oscillator strengths. Though $\langle r^2 \rangle$ values reveal that these states have spatial extensions similar to Rydberg-like states, they in fact have strong contribution of $\pi-\pi^*$ transitions and their calculated dipole moments are similar to that of the ground and 1L_b $\pi-\pi^*$ states. And so, these states should be considered as valence excited states. All Rydberg states, as expected, have very small oscillator strengths.

Pratt and co-workers²⁰ recently showed that at the S_3 state ($n-\pi^*$ state) geometry, the $n-\pi^*$ state becomes the lowest excited state, lower than the 1L_b and 1L_a $\pi-\pi^*$ states, which indicates that the 1L_b $\pi-\pi^*$ and $n-\pi^*$ states cross one another at some geometry. The study also revealed that the respective minimum on the $\pi-\pi^*$ and $n-\pi^*$ potential energy surfaces is separated by around 0.35 eV. With these results, the authors concluded that as the vibrationally excited S_1 state is energetically close to the S_3 minimum, significant state mixing is possible. This mixing of the states would result in the significant change in the magnitude and direction of the dipole moment, which has been observed experimentally.²⁰ Interestingly, the $\pi-\sigma^*$ state calculated in the present study lies just 0.22 eV above the $n-\pi^*$ state (Table II). So even if the former state does not mix with the 1L_b $\pi-\pi^*$ state directly, it may mix with this 1L_b state indirectly through by mixing with the $n-\pi^*$ state.

To examine this possibility and to check the importance of the other states in the photophysics of the azaindole molecule, we further studied the 1L_b $\pi-\pi^*$, $n-\pi^*$, and $\pi-\sigma^*$ states. At first, we optimized these three excited states by using CAM-B3LYP functional⁵⁶ with 6-311+G(*d,p*) basis set [Cartesian coordinates in the supplementary material (Ref. 43)] and then, we obtained the final energies of these states using SAC-CI (LevelThree) theory with the same basis set combinations (cc-pVTZ for carbon and nitrogen atoms, cc-pVDZ, for hydrogen atoms, and augmented with two sets of Rydberg *spd* functions for carbon and two sets for nitrogen atoms), which was used earlier for the vertical excitation energy calculations. The molecule remains planar during the unconstrained structure optimization of each electronic state, and therefore, some of the minima obtained here may not correspond to true global minima, but should be a close approximation to them. The results are given in Table III.

Table III shows some exciting facts. First, as predicted by Pratt and co-workers recently,²⁰ $n-\pi^*$ state is the lowest excited state (1st excited state) at the $n-\pi^*$ optimized geometry, which

TABLE III. Energies (related to the ground state minimum energy), in eV, of the important excited electronic states at the optimized geometries of 1L_b , $^1(n-\pi^*)$, and $^1(\pi-\sigma^*)$ states.

State	At ground state optimized structure	At $^1A'$ 1L_b ($\pi-\pi^*$) optimized structure	At $^1A''$ $n-\pi^*$ optimized structure	At $^1A''$ $\pi-3s$ and $\pi-\sigma^*$ optimized structure
Ground state		0.20	0.77	0.57
1L_b ($\pi-\pi^*$)	4.03	3.95	4.79	4.81
1L_a ($\pi-\pi^*$)	4.23	4.37	5.08	4.40
$n-\pi^*$	4.61	4.86	4.31	
$\pi-3s$ and $\pi-\sigma^*$	4.83	5.13	5.58	4.83

means this state crosses the 1L_b state at some geometry. Also, as mentioned in that earlier study,²⁰ the energy difference between the respective minima on the potential energy surfaces of these two states is as small as 0.36 eV. Hence, mixing of these two states is highly possible. Such mixing of two states with different symmetries is possible through vibronic coupling by out-of-plane modes connecting both the states. Second, at the $\pi\text{-}\sigma^*$ state geometry, the 1L_a state becomes the lowest excited state, around 0.4 eV lower than the 1L_b state. This indicates that these two low-lying $\pi\text{-}\pi^*$ states cross each other, and hence, mixing of these two states is a significant possibility. Third, the $\pi\text{-}\sigma^*$ state becomes the first excited state in A'' symmetry group (the $n\text{-}\pi^*$ state is not found at least up to 5.5 eV), i.e., lying lower than the $n\text{-}\pi^*$ state, at the $\pi\text{-}\sigma^*$ state geometry. This reveals the fact that the $\pi\text{-}\sigma^*$ state crosses the $n\text{-}\pi^*$ state at some geometry. Both these states have A'' symmetry, and hence, state mixing is highly possible. All these results clearly indicate that all these four low-lying excited states, 1L_b and 1L_a $\pi\text{-}\pi^*$, $n\text{-}\pi^*$, and $\pi\text{-}\sigma^*$ states, cross each other and significant state mixing among all of these four states is highly likely. So the major change in the magnitude and direction of the dipole moment of the upper state vibrational level in the $0,0 + 280\text{ cm}^{-1}$ band in the $S_1 \leftarrow S_0$ transition when compared to those of the zero-point level of the S_1 state might arise not just because of 1L_b $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ state mixing, but as a consequence of mixing with the other two states (1L_a $\pi\text{-}\pi^*$ and $\pi\text{-}\sigma^*$) also. The higher dipole moments calculated for the latter two states (Table II) also support this finding. Thus, it is possible to say that through state mixing, and via strong vibronic coupling, all of these four low-lying states cross/mix with each other and it can be concluded that all these states actively take part in the photochemistry of azaindole monomer.

The sign of the transition dipole moment for the S_1 state is in debate, while most of the experimental studies^{18,19} support a negative value, theoretical calculations conclude otherwise.^{15,17} The present study (Figure 2) stands along with

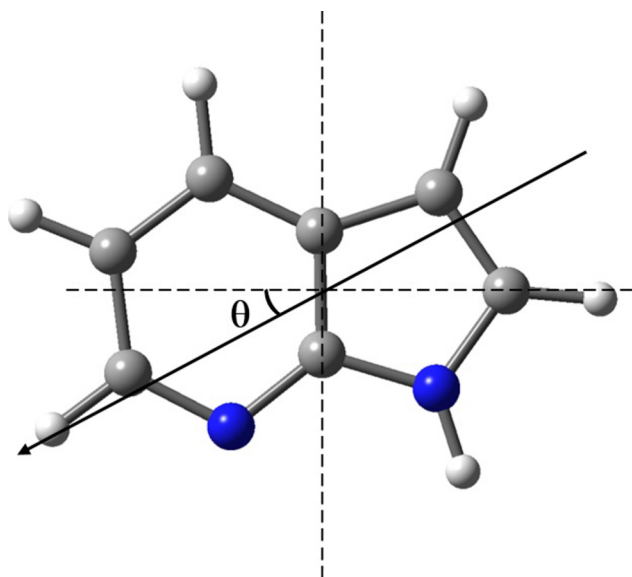


FIG. 2. The angle θ between transition dipole moment vector and the long molecular axis.

TABLE IV. Low-lying triplet excited states of azaindole and benzimidazole obtained using SAC-CI (LevelThree) with cc-pVTZ basis set for C and N, and cc-pVDZ basis set for H incorporated with Rydberg $[2s,2p]$ diffuse functions on C and N atoms at their respective CCSD/6-311+G(d,p) optimized geometries. Excitation energies (ΔE) are in eV.

Azaindole			Benzimidazole		
State	Nature	ΔE	State	Nature	ΔE
$1^3A'$	$\pi\text{-}\pi^*$ (L_a)	3.31	$1^3A'$	$\pi\text{-}\pi^*$ (L_a)	3.59
$2^3A'$	$\pi\text{-}\pi^*$ (L_b)	3.91	$2^3A'$	$\pi\text{-}\pi^*$ (L_b)	4.18
$1^3A''$	$n\text{-}\pi^*$	4.44	$3^3A'$	$\pi\text{-}\pi^*$	4.76
$3^3A'$	$\pi\text{-}\pi^*$	4.80	$1^3A''$	$\pi\text{-}3s$ and $\pi\text{-}\sigma^*$	5.02
$2^3A''$	$\pi\text{-}3s$ and $\pi\text{-}\sigma^*$	4.94	$2^3A''$	$\pi\text{-}3s$ and $\pi\text{-}\sigma^*$	5.10
$3^3A''$	$\pi\text{-}3p\sigma$ and $\pi\text{-}3s$	5.45	$3^3A''$	$\pi\text{-}3p\sigma$	5.63

the earlier theoretical works, providing a positive value. The calculated TDM for the S_1 state, $+28.2^\circ$, however, agrees well with the values (20.5° and 27°) obtained in the previous theoretical studies. Possible reason(s) behind this discrepancy between theory and experiment is not known at present.

The studied triplet states and their excitation energies are given in Table IV. The lowest excited triplet $1^3A'\pi\text{-}\pi^*$ has an L_a character as it has been assumed in the experimental study as well as predicted in the earlier theoretical studies. Phosphorescence emission of azaindole in the argon matrix shows a sharp $S_0 \leftarrow T_1$ 0-0 band at 3 eV.¹² The calculated vertical excitation energy for this state, 3.31 eV, which does not have any difference with the value calculated using the CAS-PT2 theory, 3.32 eV,¹⁵ agrees well with the experimental value. The excitation energies calculated for the $2^3A'\pi\text{-}\pi^*$ (L_b) state using SAC-CI and CAS-PT2 are 3.91 and 3.90 eV, respectively. However, such a harmony between the theories is not found for the $^3n\text{-}\pi^*$ state; the calculated SAC-CI energy, 4.44 eV, is around 0.36 eV lower than the CAS-PT2 energy. The $^3n\text{-}\pi^*$ state is close in energy with the S_1 state and in fact it is much closer to the bright state. So as Ilich¹² suggested, it could be involved in the intersystem crossing and plays a role in the enhancement of the nonradiative relaxation mechanisms and thus becomes the reason for the low phosphorescence yield in azaindole.

The results obtained for the benzimidazole molecule are listed in Table V along with the available theoretical (CAS-PT2) and experimental values. It should be noticed that all the experimental values were obtained in liquid phase and also they cannot be considered as either origin or peak maximum. The calculated transition energy for the first singlet excited state, 1L_b $\pi\text{-}\pi^*$, is around 0.25 eV smaller than the experimental value; however, the energy obtained for the 1L_a $\pi\text{-}\pi^*$ state agrees well with the experimentally derived value. As in the case of azaindole, the lowest Rydberg state ($1^1A''$) wavefunction is partially dominated by the electronic configuration $\pi \rightarrow \sigma^*$, with the σ^* orbital essentially localized on the NH moiety and having a node along the NH bond. The excitation energies obtained for the other Rydberg states are also given in the table. Interestingly, unlike in azaindole case, the $n\text{-}\pi^*$ state does not exist close in energy with the low-lying $\pi\text{-}\pi^*$ states and in fact we did not find the $n\text{-}\pi^*$ state at least up to 6.15 eV energy. So the $n\text{-}\pi^*$ state does not have any

TABLE V. Low-lying singlet excited states of benzimidazole obtained using SAC-CI (LevelThree) with cc-pVTZ basis set for C and N, and cc-pVDZ basis set for H incorporated with Rydberg [2*s*,2*p*,2*d*] diffuse functions on C and N atoms at CCSD/6-311+G(*d,p*) optimized geometry. Excitation energies (ΔE), oscillator strengths (f), second moments ($\langle r^2 \rangle$), and dipole moments (μ).

State	Nature	SAC-CI			ΔE (eV)		
		ΔE (eV)	f	$\langle r^2 \rangle$	μ (D)	Other theory	Expt.
$1^1A'$	Ground state			984.4	3.62		
$2^1A'$	$\pi-\pi^*$ (L_b)	4.26	0.076	983.9	3.49	4.56 ^a	4.5 ^b
$1^1A''$	$\pi-3s$ and $\pi-\sigma^*$	4.98	0.000	1048.3	10.93		
$3^1A'$	$\pi-\pi^*$ (L_a)	5.00	0.135	989.3	3.37	4.99 ^a	5.0 ^c
$2^1A''$	$\pi-3s$ and $\pi-\sigma^*$	5.02	0.004	1048.1	10.17		
$3^1A''$	$\pi-3p\sigma$	5.53	0.002	1082.2	7.58		
$4^1A''$	$\pi-3p\sigma$	5.55	0.002	1080.0	9.04		
$4^1A'$	$\pi-3p\pi$	5.72	0.061	1059.4	2.33		
$5^1A'$	$\pi-3p\pi$	5.74	0.005	1069.9	3.61		
$5^1A''$	$\pi-3p\sigma$	5.77	0.000	1092.0	4.26		
$6^1A''$	$\pi-3p\sigma$	5.85	0.006	1096.4	3.51		
$7^1A''$	$\pi-3d\sigma$	6.15	0.001	1101.4	1.08		
$6^1A'$	$\pi-\pi^*$ and $\pi-3d\pi$	6.16	0.410	1073.3	6.59		
$7^1A'$	$\pi-3d\pi$	6.24	0.016	1130.0	4.50		
$8^1A'$	$\pi-3d\pi$	6.32	0.121	1113.4	2.74		

^aCAS-PT2 values taken from Ref. 15.

^bGroup of sharp bands from 4.46 to 4.78 eV in water,⁵⁷ isopropanol,⁵⁸ and ethanol.⁵⁹

^cGroup of broad bands from 4.95 to 5.08 eV in water,⁵⁷ isopropanol,⁵⁸ and ethanol.⁵⁹

significant role in the photochemistry of this molecule, unlike in azaindole.

IV. CONCLUDING REMARKS

The electronic spectra of the biologically important azaindole molecule were studied using SAC-CI theory with large enough basis set incorporating necessary Rydberg *spd* functions. The calculated excitation energies agree well with the available experimental values. Significantly, the vertical excitation energy (4.61 eV) obtained for the $n-\pi^*$ state, which is shown to be involved in the photochemistry of this molecule, agrees well with the experimental value (4.54 eV). The present high-level SAC-CI study reveals that in addition to the $n-\pi^*$, two other states, $^1L_a \pi-\pi^*$ and $\pi-\sigma^*$ states, also cross the lowest lying $^1L_b \pi-\pi^*$ state and mixing among all these four states is possible. This four-state mixing could have contributed to change in the magnitude and direction of the dipole moment of the upper state vibrational level in the $0,0 + 280 \text{ cm}^{-1}$ band in the $S_1 \leftarrow S_0$ transition when compared to that of the zero-point level of the S_1 state. Furthermore, as in indole, $\pi-\sigma^*$ state might also have an important role in the complicated photophysics of azaindole. Electronic structure of benzimidazole was also studied. The results agree well with the available experimental values and, unlike in azaindole, the $n-\pi^*$ state in benzimidazole is not found at least up to 6 eV energy, and thus, it may have no significant role in the photochemistry of this molecule, contrary to case in azaindole.

Finally, we show that the use of double-hybrid density functionals for the TD-DFT calculations was unable to solve the TD-DFT errors in predicting the right order of 1L_b and $^1L_a \pi-\pi^*$ states.

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