

Theoretical Studies of the Low-Lying Electronic States of Diazirine and 3,3'-Dimethyldiazirine

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The low-lying electronic states of diazirine and 3,3'-dimethyldiazirine have been studied by high level *ab initio* quantum chemical methods. The equilibrium geometries of the ground state and the first excited singlet and triplet states have been optimized using the Hartree-Fock (HF) and complete active space SCF (CASSCF) methods, as well as using the Møller-Plesset second order perturbation (MP2) theory and the single configuration interaction (CIS) theory. It was found that the first excited singlet state is of 1B_1 symmetry resulting from the $n-\pi^*$ transition, while the first excited triplet state is of 3B_2 symmetry resulting from the $\pi-\pi^*$ transition. The harmonic vibrational frequencies have been calculated at the optimized geometry of each electronic state, and the scaled frequencies have been compared with the experimental frequencies available. The adiabatic and vertical transition energies from the ground electronic state to the low-lying electronic states have been estimated by means of multireference methods based on the CASSCF wavefunctions, *i.e.*, the multiconfigurational quasi-degenerate second order perturbation (MCQDPT2) theory and the CASSCF second-order configuration interaction (CASSCF-SOCI) theory. The vertical transition energies have also been calculated by the CIS method for comparison. The computed transition energies, particularly by MCQDPT2, agree well with the experimental observations, and the electronic structures of the molecules have been discussed, particularly in light of the controversy over the existence of the so-called second electronic state.

Introduction

Diazirine and its derivatives, which are highly strained, three-membered heterocyclic molecules, have received considerable attention since the first synthesis of diazirine in the early sixties.^{1,2} The molecular structures of diazirine and several substituted diazirines have been determined by microwave and electron diffraction studies,³⁻⁶ and many spectroscopic properties including the band origins and the vibrational frequencies have been extensively studied by infrared⁷⁻⁹ and electronic absorption spectroscopy.¹⁰⁻¹⁷ With the recent development in experimental techniques, photochemical pathways followed by UV excitation have been investigated through the observation of fluorescence from alkyl diazirines in solution^{18,19} and in the gas phase.²⁰ Despite of all these efforts, however, the electronic structure of this class of molecules has not been fully understood, and in particular, whether or not there exists an electronic state near the $^1(n-\pi^*)$ state is still controversial.^{17,21} On the theoretical side, some calculations were conducted using low level *ab initio*^{16b,22,23} or semi-empirical methods.²⁴ Recently a study of diazirine using the MCSCF method has also been reported.²⁵ However, these studies focused mainly on the qualitative features of potential energy surfaces for the photochemical decomposition pathways of the diazirine-diazomethane system, and the detailed electronic structure and spectroscopic properties of the excited states have not been examined at a sufficiently high level of theory.

In the present study, the electronic structure and properties of the low-lying electronic states of diazirine (DA) and 3,3'-dimethyldiazirine (DMD) have been investigated using *ab*

initio quantum chemical methods. DA and DMD are relatively small molecules by the current standard of computation, and therefore extensive computations are possible at fairly higher level of theory than the previous studies employed. The approach used here is the complete active space SCF (CASSCF) method.²⁶ The CASSCF wavefunctions comprise all strongly interacting electronic configurations represented by the configuration state functions (CSFs), and are therefore expected to give a proper description of the major features in the electronic structure of the excited states. In order to obtain quantitatively accurate results for the electronic excitation energies, however, the dynamic electron correlation effects also have to be considered. These effects are added in a subsequent step using multiconfigurational methods with the CASSCF wavefunctions served as the reference function.

The computational methods and details are described in the next section. The calculated results and discussion then follow, and conclusions are summarized in the last section.

Computational Methods

The equilibrium geometries of the ground states and the first singlet and triplet excited states of DA and DMD were fully optimized at the Hartree-Fock (HF) and CASSCF levels, using the standard 6-31G(d) basis set. For HF calculations of the triplet states, the restricted open-shell HF (ROHF) method was used to avoid spin contamination. In addition, the geometries of the ground states were also obtained by the Møller-Plesset second-order perturbation theory (MP2), and the excited state geometries by the single configuration inter-

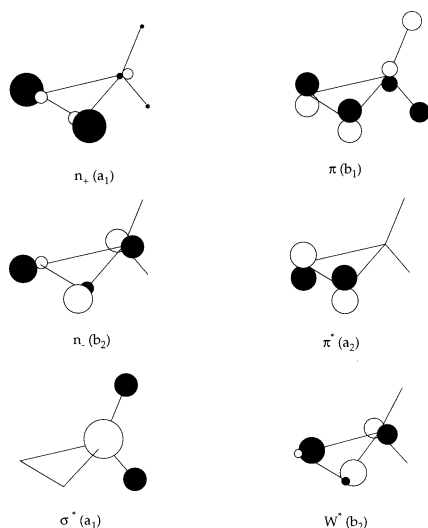


Figure 1. Schematic representation of the molecular orbitals of diazirine relevant in the present study

action (CIS) method. For CASSCF computations, the active space consists of six electrons distributed in six active orbitals, denoted as CASSCF (6,6). The same active orbitals were used for all electronic states, and they are shown in Figure 1, along with the description of the molecular orbitals (MO). All optimized structures were confirmed to be those of energy minimum by frequency calculations.

Although electron correlation is partially considered at CASSCF level, accurate determination of the energy gaps between the electronic states requires that dynamic electron correlation should be considered as well. The present study employed the multiconfigurational quasi-degenerate second-order perturbation theory (MCQDPT2)²⁷ and the CASSCF second-order configuration interaction (CASSCF-SOCI) theory²⁸ in order to account for dynamic electron correlation, which use the CASSCF wavefunctions as the reference function. For calculations of the adiabatic transition energies, the electronic energies of each electronic state were calculated by the MCQDPT2 or CASSCF-SOCI method at the geometries of each electronic state optimized at CASSCF level, while the vertical transition energies were calculated at the ground state geometry obtained at CASSCF level. Also the vertical transition energies were calculated for comparison using the CIS method at the MP2 geometry of the ground state. For calculations of the transition energies, the same 6-31G(d) basis set was used as in geometry optimizations and frequency calculations. This basis set lacks diffuse functions, and therefore the Rydberg states cannot be treated with high accuracy. We focused mainly in the present study on the valence excited states, and the proper treatment of the Rydberg states is the subject of further study.

All quantum chemical calculations were performed using the GAMESS²⁹ and Gaussian 94³⁰ packages. Both packages include the HF, MP2, and CASSCF modules and produce equivalent results. The MCQDPT2 and CASSCF-SOCI calculations were conducted with the modules implemented in GAMESS, while the CIS calculations with the one in Gauss-

ian 94.

Results and Discussion

DA and DMD molecules belong to symmetry point group C_{2v} .^{3,4} For the purpose of reference, the C_2 axis is chosen to correspond to the z axis, and the three-membered ring to lie in the yz plane. In order to discuss the electronic structure of DA and DMD, a brief description of a few highest occupied and lowest unoccupied MO's relevant in the present study will be given first. Schematic representation of these MO's of DA is shown in Figure 1, and the MO's of DMD are similar to those of DA. The highest occupied MO (HOMO) of both DA and DMD is a nonbonding orbital, denoted by $n_-(b_2)$. The next lower orbitals are a $\pi(b_1)$ MO in the N=N bond and a nonbonding MO, denoted by $n_+(b_1)$, in the order of decreasing energy. The lowest unoccupied MO (LUMO) is a $\pi^*(a_2)$ orbital, and the next higher virtual orbital is a $\sigma^*(a_1)$ MO, mainly localized at the carbon in the ring. The third virtual MO is of Walsh-type MO, $W^*(b_2)$.

The optimized geometries and the total electronic energies of DA and DMD are presented in Tables 1 and 2, respectively. The structural parameters for the ground states of DA and DMD have been determined from microwave spectroscopy.^{3,4} The calculated geometries for the ground states of both molecules are in good agreement with the experimental ones, although a slightly larger discrepancy is observed in the N-N bond lengths obtained at the HF and MP2 levels, and in the C-N bond lengths obtained at the HF level. The first excited singlet states of DA and DMD were found to be a 1B_1 state resulting from the $n_-\pi^*$ transition, as expected. The CASSCF calculation predicted the first excited singlet states of both DA and DMD to be of C_{2v} symmetry, while the CIS level of theory found an energy minimum structure at C_s symmetry; at CIS level, optimizing the molecules with C_{2v} constraint always results in a structure that yields an imaginary frequency. Therefore CASSCF calculations with different active spaces were attempted to test if the structure optimized varies with the active spaces. But the structures obtained are all of C_{2v} symmetry, regardless of the active spaces used. The first excited triplet states of DA and DMD were turned out to be a 3B_2 state resulting from the $\pi-\pi^*$ transition. At the optimized geometries of the triplet states, the order of the n_- and π orbitals is reversed, and consequently the 3B_1 state resulting from the $n_-\pi^*$ transition becomes higher in energy than the 3B_2 state. The geometries optimized for the excited triplet states of DA and DMD were of C_{2v} symmetry at all levels of theory, although the CIS level of theory could not find the minimum structure for DMD. However, at the CASSCF level, we found two minimum structures for the triplet states of both DA and DMD. The first ones are very similar to those obtained from the ROHF or CIS level, and also to that found by Yamamoto *et al.*²⁵ The second ones, which have the distinctively larger N-N bond lengths than the other one, have lower electronic energies and appear to correspond to the true minima on the triplet potential energy surfaces. Therefore these second

Table 1. Optimized Equilibrium Structures^a and Total Energies^b of Low-Lying Electronic States of Diazirine

level	Ground state (¹ A ₁)				Excited singlet state (¹ B ₁)		Excited triplet state (³ B ₂)		
	CASSCF	MP2	HF	Expt. ^c	CASSCF	CIS ^d	CASSCF	CIS	ROHF
total energy	-147.940371	-148.289057	-147.836092		-147.765614	-147.679741	-147.815551	-147.757134	-147.762216
R(N-N)	1.217	1.257	1.194	1.228±0.003	1.236	1.261	1.638	1.499	1.507
R(C-N)	1.497	1.482	1.446	1.482±0.003	1.648	1.652	1.411	1.405	1.404
R(C-H)	1.071	1.082	1.074	1.09±0.02	1.066	1.371 1.076	1.082	1.079	1.080
θ(NCN)	48.0	50.2	48.8	48.6	44.0	48.2	71.0	64.5	64.9
θ(CNN)	66.0	64.9	65.6	65.7	68.0	77.7	54.5	57.8	57.6
θ(NCH)	117.1	117.2	117.9	118.2	115.2	54.1 120.8	116.3	116.7	116.9
θ(HCH)	120.3	119.4	118.0	117±2	125.3	113.8 117.5	114.0	115.8	115.2

^aBond lengths are in Å and angles in degrees. ^bEnergies are in hartrees. ^cReference 3. ^dThe CIS level of theory predicts the first excited singlet state to be of C_s symmetry.

Table 2. Optimized Equilibrium Structures^a and Total Energies^b of Low-Lying Electronic States of 3,3'-Dimethyldiazirine

level	Ground state (¹ A ₁)				Excited singlet state (¹ B ₁)		Excited triplet state (³ B ₂)	
	CASSCF	MP2	HF	Expt. ^c	CASSCF	CIS ^d	CASSCF	ROHF
total energy	-226.021655	-226.636210	-225.917872		-225.857329	-225.776727	-225.900331	-225.847001
R(N-N)	1.223	1.267	1.201	1.235±0.005	1.240	1.263	1.638	1.512
R(C-N)	1.496	1.481	1.445	1.490±0.01	1.643	1.660	1.417	1.409
R(C-C*) ^e	1.505	1.502	1.510	1.499±0.01	1.488	1.385 1.497	1.519	1.518
R(C-H)	1.086	1.095	1.086	1.100±0.01	1.087	1.088	1.084	1.084
θ(NCN)	48.3	50.6	49.1	48.9	44.3	1.080 48.0	70.6	64.9
θ(CNN)	65.9	64.7	65.5	65.5	67.8	77.5	54.7	57.5
θ(NCC*)	117.7	117.5	118.4		115.8	54.5 120.0	115.6	116.2
θ(C*CC*)	118.9	118.5	117.0	119.7±0.5	123.9	114.7 118.4	116.1	116.8

^aBond lengths are in Å and angles in degrees. ^bEnergies are in hartrees. ^cReference 4. ^dThe CIS level of theory predicts the first excited singlet state to be of C_s symmetry. ^eC* represents the carbon in methyl groups.

structures were presented for the triplet states of DA and DMD in Tables 1 and 2, respectively.

Comparing the geometries of DA and DMD, it appears that substitution by methyl groups does not affect much the structure of the three-membered ring in all electronic states, and both molecules display similar variations in their geometries with the electronic states. That is, the N-N bond lengths of both molecules become longer in the excited electronic states, particularly in the triplet excited states where the N-N bond has a single bond character rather than the double bond character. The C-N bond lengths are considerably lengthened in the excited singlet states, while they become slightly shorter in the excited triplet states. Also it is observed that both the H-C-H angle in DA and the C-C-C angle in DMD increase in the excited singlet states.

The harmonic frequencies were calculated at each optimized geometry of the electronic state, but the frequencies

obtained at the present level of theory are known to be overestimated due to anharmonicity and insufficient correction for electron correlation.^{31,32} Therefore these frequencies need to be scaled in order to compare with the experimental frequencies, and in the present study the scale factors were chosen by minimizing the differences between the calculated and experimental frequencies of the ground states in a least squares manner. Experimental frequencies for the excited states were not used because these frequencies appear to have some uncertainties as discussed below. Such scaled frequencies for DA and DMD are listed in Tables 3 and 4, respectively, along with the experimental frequencies. Agreements between the scaled and experimental frequencies are generally good, although some discrepancies are observed particularly in the excited states. As mentioned earlier, for DA and its derivatives, the existence of the second electronic state near the first excited singlet state has been assumed for

Table 3. Vibrational Frequencies^{a,b} of Low-Lying Electronic States of Diazirine

symmetry	mode	Ground state (¹ A ₁)						Excited singlet state (¹ B ₁)			Excited triplet state (³ B ₂)
		CASSCF		MP2		Expt. ^c		CASSCF		Expt. ^d	CASSCF
		frequency	intensity	frequency	intensity	frequency	intensity	frequency	intensity	frequency	frequency
a ₁	v ₁	3026	0.111	3062	0.260	3020	m	3080	0.002		2939
	v ₂	1639	0.648	1523	0.537	1626	s	1595	0.013	1488	1431
	v ₃	1451	0.062	1434	0.459	1458	s	1378	0.072	1391	1150
	v ₄	935	0.057	1003	0.091	991	m	633	0.067	791	536
a ₂	v ₅	929	0.000	969	0.000			355	0.000		910
b ₁	v ₆	3141	0.392	3181	0.572	3131	m	3233	0.004		3007
	v ₇	1073	0.117	1116	0.140	1125	m	953	0.037		840
b ₂	v ₈	933	0.782	986	0.846	967	s	574	0.665		1212
	v ₉	755	0.242	794	0.408	807	m	138	0.000		937

^aFrequencies are in cm⁻¹, and intensities in Debye²/amu-Å². ^bThe scale factors are 0.904 for CASSCF and 0.951 for MP2. ^cReference 7. ^dReference 11.

Table 4. Vibrational Frequencies^{a,b} of Low-Lying Electronic States of 3,3'-Dimethyldiazirine

symmetry	mode	Ground state (¹ A ₁)						Excited singlet state (¹ B ₁)				Excited triplet state (³ B ₂)
		CASSCF		MP2		Expt. ^c	Expt. ^d	CASSCF		Expt. ^e	Expt. ^d	CASSCF
		frequency	intensity	frequency	intensity	frequency	frequency	frequency	intensity	frequency	frequency	frequency
a ₁	v ₁	2975	0.653	3049	0.305			3015	0.103			2988
	v ₂	2899	0.737	2949	0.382			2899	0.625			2913
	v ₃	1614	0.855	1498	0.005	1603	1565	1566	0.146	1477	1477.5	1481
	v ₄	1484	0.204	1453	0.778	1458		1468	0.147	1198	1421.9	1415
	v ₅	1425	0.009	1400	0.010	1391	1389	1420	0.006	1167		1283
	v ₆	1235	0.006	1223	0.004	1136	1235	1173	0.277	997	1166.8	1004
	v ₇	964	0.049	980	0.085	988	979	888	0.005	933	934.4	739
	v ₈	671	0.000	706	0.004	738	716	509	0.013	657	656.9	487
	v ₉	353	0.006	343	0.008	433	405	324	0.019	485	280.2	320
a ₂	v ₁₀	2945	0.000	3024	0.000			2938	0.000			2974
	v ₁₁	1466	0.000	1463	0.000			1455	0.000			1468
	v ₁₂	1001	0.000	998	0.000			954	0.000			986
	v ₁₃	388	0.000	392	0.000			245	0.000			326
	v ₁₄	99	0.000	133	0.000		123.5	64	0.000		98.2	182
b ₁	v ₁₅	2974	0.405	3049	0.148			3012	0.145			2987
	v ₁₆	2894	0.461	2946	0.254			2891	0.136			2909
	v ₁₇	1475	0.056	1473	0.079			1458	0.050			1465
	v ₁₈	1420	0.232	1397	0.491			1416	0.289			1396
	v ₁₉	1219	0.318	1241	0.313			1252	0.229			1129
	v ₂₀	953	0.012	949	0.015			952	0.003			938
	v ₂₁	410	0.227	430	0.217			358	0.238			359
	v ₂₂	2948	1.426	3026	0.623			2942	0.874			2979
b ₂	v ₂₃	1481	0.277	1479	0.348			1469	0.372			1488
	v ₂₄	1108	0.000	1128	0.023			1023	0.010			1185
	v ₂₅	743	0.047	769	0.037			301	0.006			875
	v ₂₆	335	0.005	361	0.011			262	0.011			393
	v ₂₇	131	0.008	150	0.001			40	0.009			214

^aFrequencies are in cm⁻¹, and intensities in Debye²/amu-Å². ^bThe scale factors are 0.904 for CASSCF and 0.951 for MP2. ^cReference 8. ^dReference 20b. ^eReference 13.

some time.^{11-14,16} But recent studies indicate that for difluorodiazirine and DMD, this second electronic state is really a hot band,^{17,21} and the present study also did not find the evi-

dence of this so-called second electronic state. Therefore earlier vibrational analysis from electronic absorption spectra of DA and related molecules¹¹⁻¹⁴ may need reexamina-

tion, and the scaled frequencies obtained here are expected to provide reasonable estimates for the undetermined frequencies.

Accurate estimation of the energy gaps between the electronic states requires more rigorous treatments of electron correlation than provided by the CASSCF method. The most accurate way to include the dynamic correlation effects is probably provided by the multireference configuration interaction (MRCI) technique. However the applicability of the technique becomes severely limited, except for small molecular systems, because the order of the Hamiltonian matrix increases rapidly for larger systems. Rather we employed the MCQDPT2 method developed by Nakano,²⁷ which is one of the second-order perturbation theories based on the MCSCF reference functions. This technique is more efficient than the other multireference based methods such as MRCI and multireference coupled cluster methods, and moreover it can describe open shell or excited states as well as closed shell states in a single framework. The CASSCF-SOCI method was also used to calculate adiabatic transition energies, wherein all single and double excitations from the CASSCF active orbital space into the virtual orbital space are permitted. The adiabatic transition energies obtained by the MCQDPT2 and SOCI methods are presented in Table 5, along with the experimentally observed band origins of the excited states of DA and DMD. The adiabatic energies estimated using the MCQDPT2 method agree quite well with the experimental data, especially when the zero point energy is corrected, while the transition energies from the CASSCF-SOCI calculations show rather large deviation, probably due to the insufficient number of CSFs. However, the larger active space could not be used because the number of configurations generated becomes quickly too large beyond our computational resources.

For DA and related molecules, the existence of the so-called second electronic state near the 1B_1 ($n-\pi^*$) state has been the subject of some controversy. In the earlier investigation of the electronic absorption spectra,^{11-14,16} the apparent second electronic state was observed within a few hundred wavenumbers from the 1B_1 state and tentatively assigned to the 3B_2 ($\pi-\pi^*$) state, while recent studies of difluorodiazirine and DMD^{17,21} suggest that the feature is not another electronic state, but a hot band which belongs to the 1B_1 state. The adiabatic transition energies presented in Table 5 also indicate that there is no electronic state within a few hundred wavenumbers from the 1B_1 ($n-\pi^*$) state, and the 3B_2 ($\pi-\pi^*$) or 3B_1 ($n-\pi^*$) state cannot be responsible for the apparent second origin because both triplet states were found to be much lower in energy (over 0.6 eV) than the 1B_1 state. We note that for DA and DMD, the lowest triplet states are the 3B_2 ($\pi-\pi^*$) state, and the 3B_1 ($n-\pi^*$) states are slightly higher in energy than the 3B_2 state, unlike usually expected. Thus reexamination of the electronic spectra based on the present results appears to be warranted. It is also seen that the transition energies of DMD are smaller than those of DA.

Table 6 presents the vertical transition energies based on the MCQDPT2 calculations. Also the CIS calculations were

Table 5. Adiabatic Transition Energies for Diazirine and 3,3-Dimethyldiazirine

(a) diazirine					
level	MCQDPT2		CASSCF-SOCI		Expt.
state	total energy (hartree)	ΔE (eV)	total energy (hartree)	ΔE (eV)	ΔE (eV)
S ₀ (1A_1)	-148.2837697	0	-147.9988517	0	
S ₁ (1B_1)	-148.1380459	3.97 (3.85) ^a	-147.8370796	4.40	3.84 ^b
T ₁ (3B_2)	-148.1747081	2.97 (2.92)	-147.8824284	3.17	
T ₂ (3B_1)	-148.1609229	3.34 (3.18)	-147.8543029	3.93	
(b) dimethyldiazirine					
level	MCQDPT2		CASSCF-SOCI		Expt.
state	total energy (hartree)	ΔE (eV)	total energy (hartree)	ΔE (eV)	ΔE (eV)
S ₀ (1A_1)	-226.6303620	0	-226.0801973	0	
S ₁ (1B_1)	-226.4999014	3.55 (3.47) ^a	-225.9303219	4.08	3.46 ^{c,d}
T ₁ (3B_2)	-226.5263551	2.83 (2.78)	-225.9674566	3.07	
T ₂ (3B_1)	-226.5230131	2.92 (2.87)	-225.9489268	3.57	2.94 ^c

^aThe values in parenthesis are the energies with the zero point energy corrected. ^bReference 11. ^cReference 13. ^dReference 20b.

performed since the CIS method was claimed to provide reasonable estimates for the electronic energies rather inexpensively.³³ The vertical energies using the MCQDPT2 method were obtained by the two different procedures. The first procedure involves optimization of the CASSCF orbitals for each electronic state separately, and subsequent perturbational correction for electron correlation. The results from this procedure are listed under the heading of 'Nstate = 1' in Table 6. In the second procedure, the state-averaged CASSCF orbitals for the several, three in the present case, electronic states of the same symmetry were obtained and these orbitals were used for the subsequent MCQDPT2 calculations. The results are listed under the heading of 'Nstate = 3' in Table 6. This second procedure includes the interactions among the electronic states of the same symmetry to give more accurate descriptions of the electronic structures, although the use of the state-averaged orbitals may introduce a certain degree of inaccuracy.

Unlike the adiabatic transition energies, at the ground state geometries of DA and DMA, the 3B_1 ($n-\pi^*$) states are found out to be lower in energy than the 3B_2 ($\pi-\pi^*$) states at both the MCQDPT2 and CIS levels. Although the two procedures of MCQDPT2 calculations yield comparable results for other electronic states, the relative ordering of the 1B_2 and 1A_2 states in DA turns out to be different between the two procedures. That is, the first procedure predicts the 1B_2 state to be lying higher than the 1A_2 state, while the second procedure reverses this order. This suggests that for the 1B_2 or 1A_2 state, the electronic interactions between the states of the same symmetry are important, and accordingly they affect the relative orders of the electronic states. In fact, close examination of the coefficients of the CSFs indicates that the 1B_2 ($\pi-\pi^*$) and 1B_2 ($n-\sigma^*$) states are strongly mixed with each other, and cannot be described by a single configura-

Table 6. Vertical Transition Energies (eV) for Diazirine and 3,3'-Dimethyldiazirine

(a) diazirine

state	MCQDPT2 (Nstate=1)	MCQDPT2 (Nstate=3)	CIS
3B_1 ($n_- \rightarrow \pi^*$)	3.35	3.37	3.07
1B_1 ($n_- \rightarrow \pi^*$)	4.01	4.01	4.15
3B_2 ($\pi \rightarrow \pi^*$)	5.34	5.46	3.30
3A_2 ($n_+ \rightarrow \pi^*$)	6.23	5.97	5.36
3A_1 ($n_- \rightarrow W^*$)	6.66	6.57	6.87
1A_2 ($n_+ \rightarrow \pi^*$)	7.47	7.79	7.05
1B_2 ($\pi \rightarrow \pi^*$)	8.09	7.16 ^{†a}	7.94
3B_2 ($n_- \rightarrow \sigma^*$)	8.55	8.87	11.20
1A_1 ($n_- \rightarrow W^*$)	9.47	9.91 [†]	11.11
1B_2 ($n_- \rightarrow \sigma^*$)		9.99 [†]	11.67
3B_1 ($n_- \rightarrow \pi^*$; $n_- \rightarrow W^*$)		10.24	
1A_1 ($n_-^2 \rightarrow \pi^{*2}$)		10.40 [†]	
3A_2 ($\pi \rightarrow W^*$)		10.81	10.06
3A_2 ($n_- \rightarrow \pi^*$; $\pi \rightarrow \pi^*$)		10.87	
1A_2 ($\pi \rightarrow W^*$)	10.99	11.23	10.62
1B_1 ($n_- \rightarrow \pi^*$; $n_- \rightarrow W^*$)		11.47	
3B_1 ($\pi \rightarrow \sigma^*$)	11.88		
1B_1 ($\pi \rightarrow \sigma^*$)	12.50		

(b) dimethyldiazirine

state	MCQDPT2 (Nstate=1)	MCQDPT2 (Nstate=3)	CIS
3B_1 ($n_- \rightarrow \pi^*$)	2.98	2.98	2.69
1B_1 ($n_- \rightarrow \pi^*$)	3.62	3.59	3.72
3B_2 ($\pi \rightarrow \pi^*$)	5.25	5.38	3.14
3A_2 ($n_+ \rightarrow \pi^*$)	6.10	5.68	5.21
3A_1 ($n_- \rightarrow W^*$)	6.75	5.80	7.12
1A_2 ($n_+ \rightarrow \pi^*$)	7.31	7.22	6.83
1B_2 ($\pi \rightarrow \pi^*$)	7.47	7.51 ^{†a}	7.68
3B_2 ($n_- \rightarrow \sigma^*$)	8.36	8.76	
1A_1 ($n_-^2 \rightarrow \pi^{*2}$)		9.35	
1A_2 ($\pi \rightarrow W^*$)	11.22	9.47 [†]	10.92
3A_2 ($\pi \rightarrow W^*$)		9.50 [†]	10.32
1B_1 ($n_- \rightarrow \pi^*$; $n_- \rightarrow W^*$)		9.93	
1A_1 ($n_- \rightarrow W^*$)		10.07	11.02
3B_1 ($n_- \rightarrow \pi^*$; $n_- \rightarrow W^*$)		10.42	
1A_2 ($n_- \rightarrow \pi^*$; $\pi \rightarrow \pi^*$)		10.79 [†]	
3A_2 ($n_- \rightarrow \pi^*$; $\pi \rightarrow \pi^*$)		10.92 [†]	
3B_1 ($\pi \rightarrow \sigma^*$)	11.92		
1B_1 ($\pi \rightarrow \sigma^*$)	12.27		

^aThe states marked with the dagger symbol are mixed strongly with the state of the same symmetry.

tion. Besides these, there are some other electronic states that are strongly mixed with those of the same symmetry and represented by more than one configuration. Such electronic states are marked with the dagger symbol in Table 6. The CIS transition energies are comparable to those of MCQDPT2 in the low energy region, but for the higher-lying states the discrepancies become noticeable. This is probably due to the

limitation of the CIS method in describing the complexity of excited state wavefunctions.³⁴ The CIS approach is based on a CI calculation in the CSF space singly excited with respect to a ground state. However some of the excited states have a multi-excited character, and cannot be described by single excitations only. As for the existence of the second electronic state near the 1B_1 ($n_- \rightarrow \pi^*$) state, the vertical transition energies also do not support the presence of such a state, and this electronic state is probably a misinterpretation of the electronic spectra, as recent experimental studies suggest.^{17,21}

Although present determination of the adiabatic and vertical transition energies may provide the overall picture of the electronic structures of DA and DMD, the basis set and the active space used in the present study are not large enough to describe subtle details of the nature of the excited states, particularly the diffuse character of some of the excited states, and the interactions of them. More rigorous study of the electronic structures of DA and its derivatives is underway using the extended basis sets and the large active spaces than in the present study. Through this study, we hope that more definite conclusions can be made regarding the full interactions among the electronic states, including those between the valence and Rydberg states.

Conclusions

In the present study, the low-lying electronic states of DA and DMD have been studied by the CASSCF method, as well as the HF, MP, and CIS methods. It was found that the first excited singlet state is of 1B_1 symmetry resulting from the $n_- \rightarrow \pi^*$ transition, while the first excited triplet state is of 3B_2 symmetry resulting from the $\pi \rightarrow \pi^*$ transition. The geometries of the ground states optimized at the CASSCF level are in good agreement with the geometrical parameters obtained experimentally. For the singlet excited states, the CASSCF level of theory predicts these states to be of C_{2v} symmetry, while the CIS level of theory to be of C_s symmetry. The calculated vibrational frequencies of the ground states match well, with the appropriate scale factors, the experimental frequencies available, and the calculated frequencies for the excited states are expected to provide reasonable estimates for the unknown frequencies. The adiabatic and vertical transition energies from the ground electronic state to the low-lying electronic states have been estimated by means of multireference methods based on the CASSCF reference wavefunctions. The computed transition energies, particularly by MCQDPT2, agree well with the experimental observations, and the calculated vertical energies are expected to provide the overall picture of the electronic structures of DA and DMD. As for the existence of another electronic state near the 1B_1 ($n_- \rightarrow \pi^*$) state, we could not find the evidence for such a state and reexamination of the electronic spectra of these molecules seems to be warranted, although more detailed study is needed in order to further clarify the electronic structures of DA and its derivatives.

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