Ab Initio CASSCF Study on Doublet and Quartet States of 1,3,5-Tris(methylene)benzene and 1,3,5-Benzenetriamine Trication#

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(Received August 14, 1997)

Ab Initio CASSCF results of 1,3,5-tris(methylene)benzene (TMB) and 1,3,5-benzenetriamine trication (BTA^{3+}), which are model molecules of the actively researched triradicals with star-branched topology, are presented. This study included a geometry determination of the four low-lying states ($^4A_1''$, $^4A_2$, $^2A_2$, $^2B_1$) of TMB and BTA^{3+}. The doublet–quartet splitting energies (ΔE_{D-Q}) of TMB and BTA^{3+} were calculated to be 12.7 and 3.1 kcal mol^{-1}, respectively. Furthermore, the doublet-doublet splitting energies of TMB and BTA^{3+}, which arise from a Jahn–Teller distortion of the doubly degenerate $^2E''$ state, were suitably estimated to be 2.5 and 6.8 kcal mol^{-1}, respectively, due to obviation of the spin-contamination problem. As a result of configuration mixing, it was found that the doublet states for TMB and BTA^{3+} have to be represented at least by two configurations or more. In addition, the doublet states of TMB were regarded as being a doublet triradical, while those of BTA^{3+} were close to a doublet monoradical; associated with this result, the lowest doublet states of TMB and BTA^{3+} were found to be $^2A_2$ and $^2B_1$, respectively.

In recent years there has been much interest in kinetically and thermally stable high-spin organic radicals in connection with the exploitation of organic magnets.[1,2] Diradicals are common intermediates of chemical reactions and have received perpetual attention over the past years.[3] Several diradical systems have been characterized to be ground-state triplets.[2,3] Theoretically, Borden and Davidson confirmed the topology rules predicting the spin preference of the alternant hydrocarbon π-systems.[3,4] Non-Kekulé-type hydrocarbons cannot be written by the usual Kekulé structures, and thereby have nonbonding molecular orbitals (NBMOs) that house unpaired electrons. If the NBMOs of diradicals are *nondisjoint*, which means that they span common atoms, the triplet states lie well below the singlet states.[4] The concept is equivalent to an appropriate choice of a spacer connecting between radical centers, what is called a ferromagnetic coupling unit. In particular, the most effective ferromagnetic coupling unit is *m*-phenylene.[2] In simple Hückel MO theory, the prototype diradical, *m*-benzoquinodimethane (*m*-BQDM), has two degenerate *nondisjoint* NBMOs; according to Hund's rule, the two frontier electrons separately occupy these two NBMOs, leading to a ground-state triplet.

Although there have been a large number of theoretical studies on diradicals,[3] detailed theoretical investigations on triradicals have not been carried out to the best of our knowledge. As shown in Fig. 1, triradicals with potentially strong ferromagnetic coupling, which are homologous to *m*-BQDM,

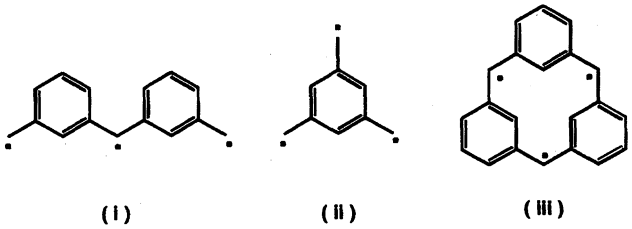

Fig. 1. Three types of *m*-phenylene-based high-spin triradicals: (i) "linear" arrangement; (ii) "star-branched" arrangement; (iii) "closed loop" arrangement.

are classified into three topological categories: (i) a "linear" arrangement,[5] (ii) a "star-branched" arrangement,[6—13] and (iii) a "closed loop" arrangement.[14] Several examples of triradical pertaining to these categories have been reported; quartet states are detected in all cases.[2] Of these triradicals, we have focused on the "star-branched" type. There are some reasons for this: (i) many experimental results have been reported on this type of triradicals; (ii) since these triradicals have a threefold axis of symmetry, their low-lying doublet states are affected by the static Jahn–Teller (J–T) effect; (iii) finally, we are able to extract the smallest model molecules in the above three types of triradicals in order to perform high-level ab initio MO calculations. To clarify the electronic structures of such molecules, we have examined 1,3,5-tris(methylene)benzene (TMB) and its isoelectronic system, 1,3,5-benzenetriamine trication (BTA^{3+}).[15,16] These model molecules idealize non-Kekulé-type triradicals with threefold axis of symmetry; moreover, BTA^{3+}-related radicals have been actively investigated by several researchers

This work was partly presented at "the 72th National Meeting of the Chemical Society of Japan," Tokyo, March 28—31, 1997, Abstr., No. 3PB023.

associated with the spin preference of heteroatom-containing organic radicals.[8,10—14] In particular, stable high-spin trication triradicals having the 1,3,5-benzenetriamine moiety have recently been reported;[12,13] furthermore, Stickley et al. have suggested that the observed doublet trications, which are thought to be excited states, are probably best viewed as triradicals, rather than monoradicals.[13] Although spin-containing unit in those trication species is assumed to be a semiquinone diimine radical and, hence, our model molecule BTA^{3+} is not directly related with them, it is interesting to reexamine the nature of the J–T deformed doublet states of TMB and BTA^{3+}.

As described in our previous papers,[16] planar TMB belonging to the D_{3h} point group has three NBMOs shown in Fig. 2, where the group-theoretically degenerate two $2e''$ MOs are nearly degenerate with the $2a_2''$ MO based on topological considerations of this type of alternant hydrocarbon π-system. According to Borden and Davidson's theory,[3,4] the lowest quartet state, $^4A_1''$, is qualitatively predicted to lie below the doublet states, since the NBMOs are *nondisjoint*. On one hand, since the lowest doublet states of TMB have degenerate $^2E''$ symmetry, the D_{3h} geometry is subject to a first order J–T distortion, which splits the degeneracy. The epikernel principle says that the J–T distorted molecules have local minimum structures within the maximal Abelian group symmetry.[17,18] In this case, the doublet state of TMB (and also BTA^{3+}) can be understood within C_{2v} symmetry. As a result, in the C_{2v} subgroup, the correspondence of the orbital symmetry with D_{3h} is expressed by

$$a_2'' \rightarrow b_1, \qquad e'' \rightarrow a_2 + b_1. \tag{1}$$

Hence, the degenerate doublet states are split into the $^2A_2$ and $^2B_1$ states. At the zeroth approximation, these states correspond to different occupations of the three frontier electrons into the three NBMOs, as shown in Fig. 3. The $^2B_1$ and $^2A_2$ states are described by configurations of $|\cdots 3b_1^2 4b_1^1\rangle$ and $|\cdots 3b_1^2 2a_2^1\rangle$, respectively. Furthermore, the $^2A_2$ state is also represented by two types of spin-adapted configurations:

$$|\cdots 3b_1^1 4b_1^1 2a_2^1(\beta\alpha\alpha + \alpha\beta\alpha - 2\alpha\alpha\beta)/\sqrt{6}\rangle, \tag{2}$$

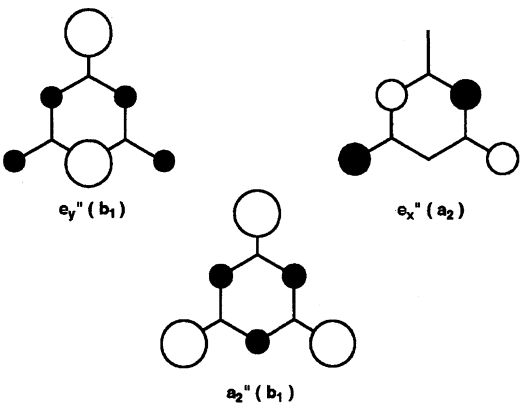

Fig. 2. Schematic representation of nonbonding MOs (NBMOs) of TMB. The symmetry classifications of the NBMOs are given for D_{3h} (C_{2v}) point group.

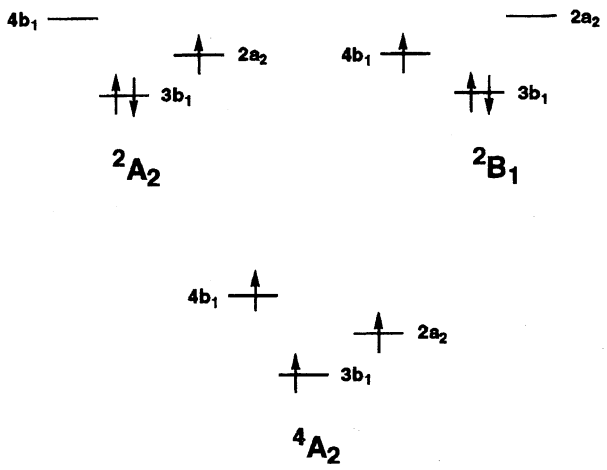

Fig. 3. Orbital occupation diagrams of the $^4A_2$, $^2A_2$, and $^2B_1$ states.

and

$$|\cdots 3b_1^1 4b_1^1 2a_2^1(\beta\alpha\alpha - \alpha\beta\alpha)/\sqrt{2}\rangle. \tag{3}$$

Herein, we classify the doublet states into two types of categories judging from the fractional occupation number estimated from the one-electron density matrix. If the doublet states are represented mainly by a configuration $|\cdots 3b_1^2 4b_1^1\rangle$ (or $|\cdots 3b_1^2 2a_2^1\rangle$), they are regarded as being *doublet monoradical*, which means that one of the three NBMOs is doubly occupied and, therefore, only one frontier electron determines the spin state of TMB (or BTA^{3+}). As the contribution of (i) the configuration arising from the two electron transition from the $3b_1$ orbital to the $4b_1$ (or $2a_2$) orbital and (ii) configurations (2) and (3) increase, the doublet states have a *doublet triradical* character, which means that the $3b_1$, $4b_1$, and $2a_2$ orbitals are occupied by one electron. Hence, we must look more carefully into the doublet states.

In this paper we report on results from ab initio calculations on the low-lying doublet and quartet states of TMB and BTA^{3+}. The study includes a geometry determination of these states. Our aim in this investigation was to identify the spin multiplicity of two molecules in the ground state, and to estimate the reliable doublet–quartet and doublet–doublet splitting energies of TMB and BTA^{3+}. The detailed electronic structures are described, particularly those for the doublet states. The most important correlation effects in the valence shell are accounted for by using the complete active space self-consistent field (CASSCF) method.[19]

Computational Details

Full geometry optimizations in C_{2v} and D_{3h} symmetry were carried out for four low-lying states ($^4A_1''$, $^4A_2$, $^2A_2$, $^2B_1$) of TMB and BTA^{3+} using the 6-31G* basis set.[20] This basis represents a compromise between completeness and economy; it includes polarization functions on non-hydrogen atoms useful for modeling radicals, and then delivers reasonable geometries and physical properties.[21] According to Ref. 22, the unrestricted Hartree–Fock (UHF) calculations seem to predict better geometries in high-spin states, due to inclusion of some electron-correlation effect. In our previ-

ous paper,[16] we have shown that the UHF wavefunctions for the $^2A_2$ state of TMB and BTA^{3+} are considerably contaminated by states of spin multiplicity higher than doublet, while those for the $^2B_1$ state are nearly in a pure doublet. This is probably because a low-lying quartet state is a $^4A_2$ state in the C_{2v} geometry constraint. This means that we cannot accurately estimate the splitting energy between two low-lying doublet states and, moreover, the doublet–quartet splitting energy. Hence, we tried to perform calculations using the spin-restricted open-shell Hartree–Fock (ROHF) method[23] as a starting point. However, we could not obtain optimized geometries for doublet states, owing to oscillatory non-convergent behavior. As described later, this suggests that the present doublet states are hardly represented by a single Slater determinant.

In order to avoid spin-contamination, and to include near-degeneracy electron correlation, we carried out CASSCF calculations, and took account of all configurations that arise when seven electrons are allowed to occupy eight π-orbitals corresponding to the eight π-MOs (CAS(7,8)). Here, we deleted the $1b_1$ π-orbital from the active space because of a smaller contribution of the excitation configuration from the $1b_1$ electrons as a result of our preliminary calculations. Thus, the active space orbitals adopted here are $1e''2a_2''2e''3e''4a_2''$ in the D_{3h} symmetry; $1a_2 2b_1 3b_1 4b_1 2a_2 5b_1 3a_2 6b_1$ (for the doublet states of BTA^{3+}, $1a_2$ and $2b_1$ orbitals are inverted) in the C_{2v} symmetry. This active space leads to 2352 configurations for the doublet states and to 1344 for the quartet states. The harmonic vibrational frequencies were calculated at the CAS(7,8)/6-31G* level to characterize the nature of the stationary points on the potential energy surfaces. All calculations were performed with the Gaussian 94 package of ab initio MO programs.[24]

Results and Discussion

Tris(methylene)benzene (TMB). Figure 4 illustrates the optimized geometries for the four low-lying states ($^4A_1''$, $^4A_2$, $^2A_2$, $^2B_1$) of TMB. In the $^4A_1''$ state, the three exocyclic C–C bonds are nearly equal to those of the benzene ring. The interior angles of the benzene ring actually deviates from 120° within the full D_{3h} geometry optimizations, while the regular hexagon was constrained in our previous calculations.[16] We could not find any nonplanar optimized structures. Although the quartet state does not have the J–T instability, we searched for quartet states within the C_{2v} symmetry; unexpectedly, the $^4A_2$ state turned out to be the lowest quartet state. However, since the deviation from the D_{3h} geometry is quite small, it is necessary to perform calculations of higher level in order to determine the ground-state geometry of TMB.[25] The calculated structures were characterized as local-minimum structures. Next, in order to estimate the spin densities on the quartet state of TMB, we performed single-point calculations using a hybrid HF (Hartree–Fock)/DF (Density Functional) method (B3LYP) that combines Becke's three-parameter nonlocal exchange functional[26–28] with the nonlocal correlation functional of

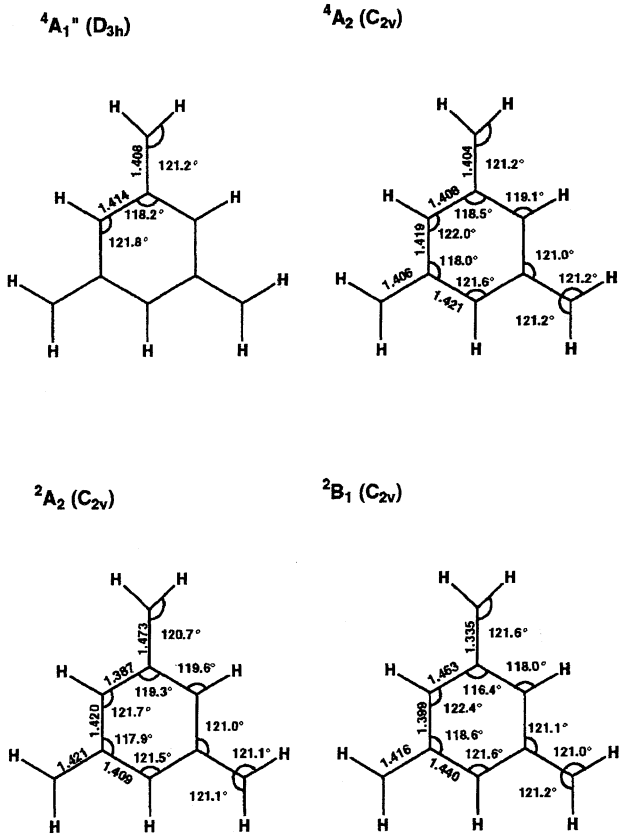

Fig. 4. Geometries of the $^4A_1''$, $^4A_2$, $^2A_2$, and $^2B_1$ states for TMB optimized at the CAS(7,8)/6-31G* level of theory. Bond lengths are in angstroms and angles in degrees.

Parr et al.[29] at each CAS(7,8)/6-31G* geometry. It is often said that density functional theory (DFT) calculations[30] give good results for both signs and magnitudes of spin densities of open-shell molecules.[31] Consequently, our calculations for the $^4A_1''$ state show a spin-polarized pattern: +0.81 on the exocyclic C atom; −0.30 and +0.60 on the *ipso* and *ortho* C atoms, respectively, to the exocyclic C atoms. Furthermore, spin densities in the $^4A_2$ state remain unchanged due to the small deviation from the D_{3h} geometry.

For the doublet states, two local minima with C_{2v} geometries were found, as indicated in our previous paper.[16] Again, we could not obtain both nonplanar local minimum points and stationary points with planar C_s symmetry. These results may support the validity of the epikernel principle.[18] One such C_{2v} geometry ($^2A_2$ state) has an "elongated" nature in which one of the peripheral C–C bonds is longer than the other two by 0.05 Å. In the UHF/6-31G calculations,[16] the elongated bond was extraordinarily long (1.502 Å) owing to inability of the UHF method to treat nondynamic correlation effects. On the whole, the benzene ring takes nearly a regular hexagonal structure and the exocyclic C–C bonds have a single bond character. In contrast, the $^2B_1$ state prefers a compressed geometry in which the one exocyclic C–C bond is shorter than the other two by 0.08 Å and has a nearly double bonding character (1.335 Å). Associated with the short exocyclic C–C bonds, the benzene ring is distorted from the

regular hexagonal structure around the *ipso* carbon atom. In particular, the ring C–C bond neighboring the short exocyclic bond is regarded as being a single bond, and the C–C–C bond angle including the *ipso* carbon atom is significantly deformed from 120°.

Table 1 lists the doublet–quartet splitting energies obtained from CAS(7,8)/6-31G* calculations and the coefficients of the dominant configurations. Although the ground state is a quartet, as predicted in the previous results,[16] the $^4A_2$ state is predicted to be the ground state of TMB, which lies 1.2 kcal mol^{-1} below the $^4A_1''$ state. The $^2A_2$ and $^2B_1$ states lie 12.7 and 15.2 kcal mol^{-1}, respectively, above the $^4A_2$ state. The doublet–quartet splitting energy (ΔE_{D-Q}) does not change dramatically compared with the UMP2/6-31G*//UHF/6-31G value of 14.5 kcal mol^{-1}.[16] On the other hand, the doublet–doublet splitting energies are considerably reduced to 2.5 kcal mol^{-1} from a UMP2 value of 22.5 kcal mol^{-1},[16] thus showing the importance of nondynamic correlation effects. This small energy splitting is reasonable because the two doublet states are originally degenerate in the D_{3h} geometry.

Let us now look at the electronic structure of each state of TMB in detail. As described in the introduction, it is worth examining whether the doublet states are regarded as a doublet monoradical or a doublet triradical. As shown in Table 1, although the quartet states are represented qualitatively with a single configuration ($|\cdots 3b_1{}^1 4b_1{}^1 2a_2{}^1\rangle$ for the $^4A_2$ state; $|\cdots 2a_2''{}^1 2e''{}^2\rangle$ for the $^4A_1''$ state), the Hartree–Fock description is no longer suitable for the doublet states. Hereafter, we discuss the doublet wavefunctions based on the calculated canonical HF orbitals, three NBMO orbitals of which are approximately represented as shown in Fig. 2. The electronic structure of the $^2A_2$ state is described with at least three configurations,

$$\Psi(^2A_2) \cong c_1|\cdots 3b_1{}^2 2a_2{}^1\rangle - c_2|\cdots 4b_1{}^2 2a_2{}^1\rangle + c_3|\cdots 3b_1{}^1 4b_1{}^1 2a_2{}^1(\beta\alpha\alpha + \alpha\beta\alpha - 2\alpha\alpha\beta)/\sqrt{6})\rangle + \cdots \quad (4)$$

The coefficients of these three configurations in the MC-SCF wave function were found to be c_1=0.58, c_2=0.60, and c_3=0.42, respectively. Since c_1 is nearly equal to c_2, the wavefunction Eq. 4 can be represented approximately as

$$\Psi(^2A_2) \cong c_1|\cdots((\phi^1\varphi^1)^{(1)}2a_2{}^1)^{(2)}\rangle + c_3|\cdots((\phi^1\varphi;^1)^{(3)}2a_2{}^1)^{(2)}\rangle, \quad (5)$$

where ϕ and φ are defined as

$$\phi = (3b_1 + 4b_1)/\sqrt{2}, \quad (6)$$

$$\varphi = (3b_1 - 4b_1)/\sqrt{2}. \quad (7)$$

Then, the third term in Eq. 4 is transformed as

$$|\cdots 3b_1{}^1 4b_1{}^1 2a_2{}^1(\beta\alpha\alpha + \alpha\beta\alpha - 2\alpha\alpha\beta)/\sqrt{6}\rangle = |\cdots((3b_1{}^1 4b_1{}^1)^{(3)}2a_2{}^1)^{(2)}\rangle = |\cdots((\phi^1\varphi^1)^{(3)}2a_2{}^1)^{(2)}\rangle. \quad (8)$$

The superscript numerals with parentheses designate the multiplicity of spin-coupling. From the above derivation, the large contribution of the double excitation configuration $3b_1 \rightarrow 4b_1$ shows that the $^2A_2$ state of TMB is a *doublet triradical*; indeed, the fractional occupation numbers of the $^2A_2$ state were calculated to be 1.91, 1.93, 0.97, 1.03, 1.00, 0.06, 0.08, 0.01. The transformed orbitals, ϕ and φ, are schematically depicted in Fig. 5(a). The φ orbital has a localized character on one exocyclic C atom, while the ϕ and $2a_2$ orbitals are delocalized over the rest of the molecular space. Therefore, one electron is localized on the longer methylene moiety and the other electrons are delocalized over the remaining *m*-benzoquinodimethane moiety.

Similarly, the $^2B_1$ state takes a *doublet triradical* electronic structure,

$$\Psi(^2B_1) \cong c_1|\cdots 2b_1{}^2 3b_1{}^2 4b_1{}^1\rangle - c_2|\cdots 2b_1{}^2 2a_2{}^2 4b_1{}^1\rangle + \cdots \quad (9)$$

Here c_1=0.64 and c_2=0.60, and thus the fractional occupation numbers of the $^2B_1$ state, were calculated to be 1.92, 1.88, 1.04, 1.01, 0.96, 0.12, 0.07, 0.00. The wavefunction Eq. 9 can be factored into the following form:

Table 1. Relative Energies of Four Low-Lying States and CI Coefficients of Dominant Configurations for TMB at the CAS(7,8)/6-31G*//CAS(7,8)/6-31G* Level of Theory

State	Energy[a)]	Configuration	Coefficient
$^4A_2$	0.0	$(1a_2)^2(2b_1)^2(3b_1)^1(4b_1)^1(2a_2)^1$	0.93
$^4A_1''$	1.2	$(1e'')^4(2a_2'')^1(2e'')^2$	0.93
$^2A_2$	12.7	$(1a_2)^2(2b_1)^2(4b_1)^2(2a_2)^1$	0.60
		$(1a_2)^2(2b_1)^2(3b_1)^2(2a_2)^1$	−0.58
		$(1a_2)^2(2b_1)^2((3b_1)^1(4b_1)^1(2a_2)^1(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6}))$	−0.42
$^2B_1$	15.2	$(1a_2)^2(2b_1)^2(3b_1)^2(4b_1)^1$	0.64
		$(1a_2)^2(2b_1)^2(4b_1)^1(2a_2)^2$	0.60

a) Energy (in kcal mol^{-1}) relative to the optimized C_{2v} quartet state, where the positive values represent that the state lies above the $^4A_2$ state; −346.0078 hartree.

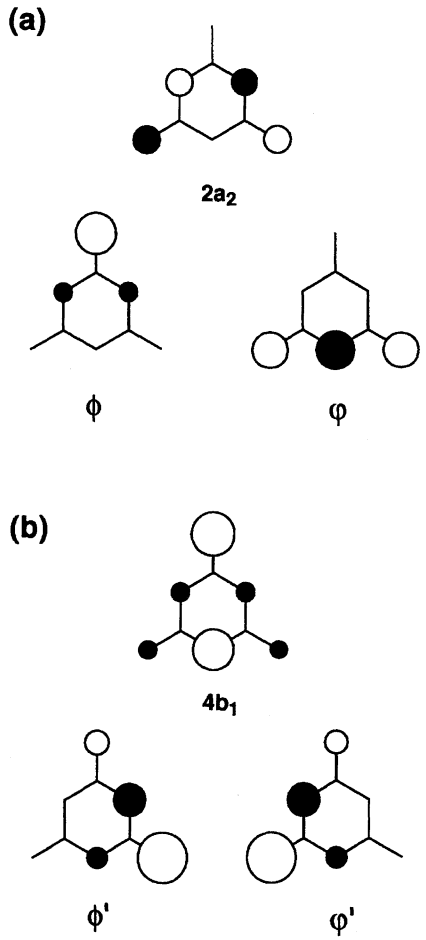

Fig. 5. Schematic representation of the transformed MOs (NBMOs) of TMB: (a) ϕ, φ, and $2a_2$ orbitals; (b) ϕ', φ', and $4b_1$ orbitals

$$\Psi(^2B_1) \cong c_1|\cdots((\phi'^1\varphi'^1)^{(1)}4b_1{}^1)^{(2)}\rangle, \quad (10)$$

where ϕ' and φ' are defined as

$$\phi' = (3b_1 + 2a_2)/\sqrt{2}, \quad (11)$$

$$\varphi' = (3b_1 - 2a_2)/\sqrt{2}. \quad (12)$$

As a result, the $^2B_1$ state of TMB is properly described by a two-configuration self-consistent-field (TCSCF) wave function. The transformed orbitals, ϕ' and φ', are schematically depicted in Fig. 5(b). Each of the two orbitals has a localized character, mainly on one exocyclic C atom, while the $4b_2$ orbitals are delocalized over the rest of the molecular space. Therefore, in the $^2B_1$ state, one electron is delocalized over the shorter methylene moiety and the phenyl ring, while the other electrons are localized separately on the remaining two exocyclic C atoms.

As mentioned above, the inability to treat the nondynamic correlation effect is the reason why the ROHF method failed in calculations of the doublet states. These results show that the spin densities in the doublet states of TMB are partly localized over one or two atoms among the three exocyclic C atoms in both the $^2A_1$ and $^2B_1$ states.

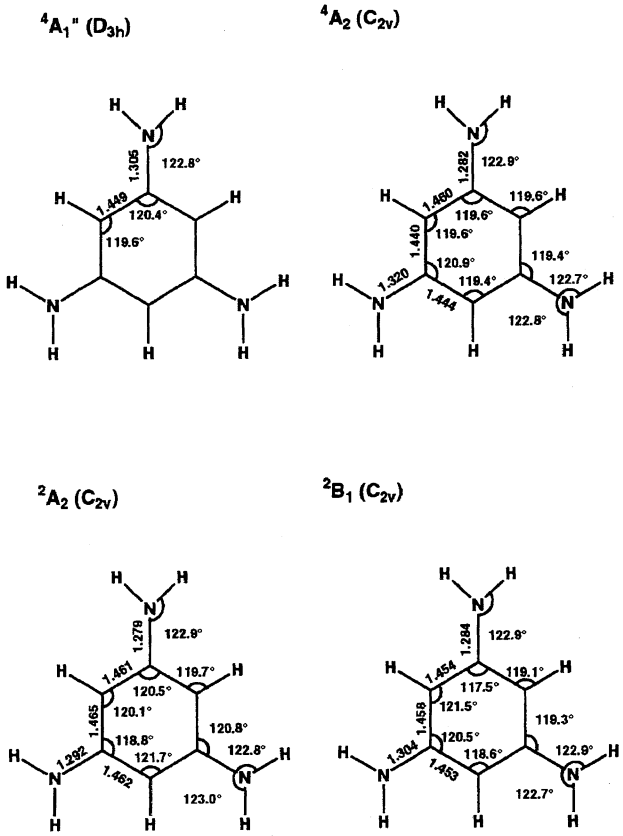

Fig. 6. Geometries of the $^4A_1''$, $^4A_2$, $^2A_2$, and $^2B_1$ states for BTA^{3+} optimized at the CAS(7,8)/6-31G* level of theory. Bond lengths are in angstroms and angles in degrees.

Benzenetriamine Trication (BTA^{3+}). The optimized bond lengths and angles for the four low-lying states ($^4A_1''$, $^4A_2$, $^2A_2$, $^2B_1$) of BTA^{3+} are shown in Fig. 6. One can see that the optimized geometries of each state of BTA^{3+} are in remarkable contrast with those of TMB. Similar to the case of TMB, the $^4A_2$ state was found to be the lowest quartet state, and has no noticeable structural change compared with the $^4A_1''$ state; thus, higher level calculations should be done in order to determine the ground-state geometry of BTA^{3+}.[25] The calculated structures were characterized as local minimum structures. Although in the previous UHF/6-31G calculations[16] the $^2A_2$ and $^2B_1$ states were characterized by "elongated" and "compressed" structures, respectively, it is difficult to classify the present CASSCF/6-31G* structures for the two doublet states from a structural point of view. Moreover, both the doublet and quartet states have a similar geometry: the central benzene ring uniformly swells up (the C–C bond lengths are around 1.45 Å.), and the exocyclic C–N bonding has nearly double bonding character. Next, we performed B3LYP/6-31G*//CAS(7,8)/6-31G* calculations for the quartet states of BTA^{3+}. As pointed out in our previous paper,[31] the spin densities over the benzene ring were found to be considerably high (−0.19 and +0.71 for the *ipso* and *ortho* C atoms to the exocyclic N atoms), while the spin density on the each exocyclic N atom was +0.54. In the $^4A_2$ state, associated with symmetry breaking, the spin densities

were calculated to be +0.50 on one N atom and +0.57 on the other N atoms. The spin densities over the benzene ring take values similar to those for the $^4A_1''$ state. We may note, in passing, that the hyperfine coupling constants (hfcc) on the exocyclic N atoms are estimated to be 9.81 G for the $^4A_1''$ state; they are 8.92 G and 10.38 G for the $^4A_2$ state.

As is the case with TMB, the ground state of BTA^{3+} was found to be a quartet (the C_{2v}-distorted $^4A_2$ state). The $^4A_1''$ state lies 0.8 kcal mol^{-1} above the $^4A_2$ state, as tabulated in Table 2. Since the ΔE_{D-Q} value was estimated to be 3.1 kcal mol^{-1}, it changes dramatically compared with the UMP2/6-31G*//UHF/6-31G value of 12.3 kcal mol^{-1}.[16] On the other hand, the $^2A_2$–$^2B_1$ splitting at the CASSCF level was calculated to be 6.8 kcal mol^{-1} (2.1 kcal mol^{-1} at the UMP2/6-31G*//UHF/6-31G level); moreover, the lowest doublet states was the $^2B_1$ state, contrary to previous predictions.[16] More noteworthy is that the $^2A_2$ state was found to be a saddle point on the potential energy surface, while the $^2B_1$ state is the local minimum point. This result suggests that the $^2A_2$ state becomes a saddle point in a pseudo-rotation pathway between the $^2B_1$ epikernel isomers.[18] However, owing to the size of the present model molecules, the intrinsic reaction coordinate (IRC) analysis has to wait for a further development of computational methods.

Turning now to the electronic structures of each state of BTA^{3+}, both the $^4A_2$ and $^4A_1''$ states involve a contribution (squared weight of $|c_1^2|$) of the main configuration ($|\cdots 3b_1{}^1 4b_1{}^1 2a_2{}^1\rangle$ for the $^4A_2$ state; $|\cdots 2a_2''{}^1 2e''{}^2\rangle$ for the $^4A_1''$ state), amounting to 0.88. Again, it was found that the doublet states are represented by the multi-configurational wavefunctions; the wavefunction Eq. 4 for the $^2A_2$ state and the wavefunction Eq. 9 for the $^2B_1$ state. However, as shown in Table 2, we should notice that the contribution from the double excitation configurations decreases below half of that from the main configuration. This tendency can be clearly seen from the fractional occupation numbers (1.93, 1.92, 1.35, 0.66, 1.01, 0.05, 0.07, 0.00) for the $^2A_2$ state and (1.93, 1.90, 1.46, 1.00, 0.56, 0.00, 0.09, 0.06) for the $^2B_1$ state. These electronic structures are certainly due to the wide energy gaps among the three NBMOs, as pointed out in our previous investigations concerning the *m*-phenylenediamine dication diradical,[32] in which opening up the gap between NBMOs leads to a closed-shell structure in the singlet state. Therefore, both of the doublet states can be viewed as a *doublet monoradical* rather than a *doublet triradical*. Associated with this change in the electronic structures, it can be explained that the $^2A_2$ state lies above the $^2B_1$ state due to an increase in the fractional occupation number into the $2a_2$ orbital. On the other hand, in TMB, the two low-lying doublet states have nearly the same fractional occupation numbers and, therefore, the splitting between the two doublet states becomes small.

Conclusions

In the present study we investigated the electronic structures of non-Kekulé triradicals with a star-branched topology, TMB and BTA^{3+}, by means of the CASSCF method. On the whole, we could remove an overestimation of the energetic stability of the $^2A_2$ state among several low-lying states, owing to considerable spin contamination in our previous UHF-based investigations. The major findings are as follows:

(1) The first of these is on the electronic ground state of TMB and BTA^{3+}. In both molecules, the quartet state with the planar C_{2v} geometry was predicted to lie below that with the planar D_{3h} geometry. However, since the geometry of the quartet ground state of this type of non-Kekulé molecule was still close to the D_{3h} geometry, higher level calculations may restore the quartet ground state of TMB and BTA^{3+} to the $^4A_1''$ state. The doublet–quartet splitting energies (ΔE_{D-Q}) of TMB and BTA^{3+} were calculated to be 12.7 and 3.1 kcal mol^{-1}, respectively. The decrease of the ΔE_{D-Q} value in BTA^{3+} seems to be related to the large gaps among three NBMOs due to heteroatom substitution, like *m*-phenylenediamine dication.

(2) The second point regards the geometries of the J–T distorted doublet states. In the $^2A_2$, the optimized structure was an "elongated" planar C_{2v} geometry in which one of the exocyclic C–C bonds is longer than the other two, while the $^2B_1$ state preferred a "compressed" planar geometry in

Table 2. Relative Energies of Four Low-Lying States and CI Coefficients of Dominant Configurations for BTA^{3+} at the CAS(7,8)/6-31G*//CAS(7,8)/6-31G* Level of Theory

State	Energy[a)]	Configuration	Coefficient
$^4A_2$	0.0	$(1a_2)^2(2b_1)^2(3b_1)^1(4b_1)^1(2a_2)^1$	0.94
$^4A_1''$	0.8	$(1e'')^4(2a_2'')^1(2e'')^2$	0.94
$^2B_1$	3.1	$(2b_1)^2(1a_2)^2(3b_1)^2(4b_1)^1$	0.80
		$(2b_1)^2(1a_2)^2(4b_1)^1(2a_2)^2$	0.47
$^2A_2$	9.9	$(2b_1)^2(1a_2)^2(3b_1)^2(2a_2)^1$	0.73
		$(2b_1)^2(1a_2)^2(4b_1)^2(2a_2)^1$	−0.44
		$(1a_2)^2(2b_1)^2((3b_1)^1(4b_1)^1(2a_2)^1(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6})$	−0.43

a) Energy (in kcal mol^{-1}) relative to the optimized C_{2v} quartet state, where the positive values represent that the state lies above the $^4A_2$ state ; −394.6601 hartree.

which one of the exocyclic C–C bonds is shorter than the other two. On the other hand, both doublet states in BTA^{3+} had a similar geometry in which the central benzene ring uniformly swelled up, and the exocyclic C–N bondings had a nearly double bonding character.

(3) The third concerns the electronic structures of the doublet states of TMB and BTA^{3+}. From the calculated configuration interaction coefficients, in TMB, both of the doublet states were predicted to have a *doublet triradical* character. However, in BTA^{3+}, it was suggested that the two doublet states were close to a *doublet monoradical*, probably due to an opening up of the energy gap among the quasi-degenerate NBMOs. Consequently, the lowest doublet state for TMB and BTA^{3+} were $^2A_2$ and $^2B_1$, respectively.

As for the doublet states of TMB and BTA^{3+}, since the splitting energy between the J–T distorted states are predicted to be small, it is interesting to examine whether a pseudorotation takes place or not.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture and it is also a part of the project of Institute for Fundamental Chemistry, supported by Japan Society for the Promotion of Science-Research for the Future Program (JSPS-RFTF96P00206). A. I. is grateful to the Research Fellowships of the JSPS for Young Scientists for financial support. Numerical calculations were partly carried out at the Supercomputer Laboratory of the Institute for Chemical Research of Kyoto University.

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