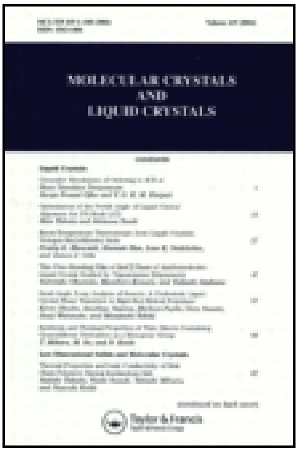

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Molecular Orbital Study on Quartet Molecules with Trigonal Axis of Symmetry

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MOLECULAR ORBITAL STUDY ON QUARTET MOLECULES WITH TRIGONAL AXIS OF SYMMETRY

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Abstract The ESR spectrum of the randomly oriented cationic triradical of 1,3,5-tris(diphenylamino)benzene (TDAB) is shown to agree well with the theoretical prediction of a quartet ($S = 3/2$) molecule. The electronic structures of non-Kekulé-type isoelectronic molecules 1,3,5-trimethylenebenzene (TMB) and 1,3,5-triaminobenzene trication (TAB^{3+}) are discussed by means of the ab initio molecular orbital (MO) method in the unrestricted Hartree-Fock scheme. In TMB the quartet state with planar D_{3h} geometry is predicted to lie 26.1 kcal/mol below the lowest doublet state with a planar C_{2v} geometry in which one of the methylene groups has a longer C-C bridge bond connecting the phenyl ring. Moreover, in TAB^{3+} the quartet state with planar D_{3h} also lies 16.9 kcal/mol below the lowest doublet state with an orthogonal geometry where one of the amino groups is twisted out of the molecular plane. These quartet ground states result from the nearly threefold-degenerate orbitals consisting of the nonbonding MOs. In addition, the quartet-doublet splitting energy of TDAB is investigated using the semiempirical AM1 method.

INTRODUCTION

Leo made the first attempt to prepare the triradical of 1,3,5-tris(diphenylmethyl)-benzene (TDMB; see Figure 1(a)).[1] Subsequently, Zimmermann et al. reported the preparation[2] of 1,3,5-tris(di-*p*-biphenylmethyl)benzene (TDBMB) and the observation[3] of a quartet ground state by magnetic susceptibility measurements. The ESR spectrum of the quartet state of this triradical was discussed by Brickmann and Kothe.[4] Recently, we have shown that the ESR spectrum of the cationic triradical of 1,3,5-tris(diphenylamino)benzene ($TDAB^{3+}$; see Figure 1(b)), which has not yet been isolated, agrees well with the theoretical prediction for a quartet molecule with a trigonal axis of symmetry.[5,6]

TDMB and $TDAB^{3+}$ belong to the group of, what is called, non-Kekulé-type molecules,[7] in which no classical structures can be written, being chemically a very interesting subject. The intramolecular ferromagnetic couplings in these molecules are ascribed to the existence of a certain number of nonbonding molecular orbitals (NBMOs). In particular, alternant hydrocarbons, where the conjugated atoms are alternately labeled "star" and "unstar" such that no two atoms of the same label are directly linked, has (n^* - n) NBMOs, and exist as an (n^* - n)-fold radical, having (n^* - n) unpaired electrons occupying the NBMOs.[7] In addition, the ground state of such alternant hydrocarbons has a total spin quantum number $S = (n^* - n)/2$.[8] These theorems provide a guiding principle important for the molecular design of high-spin organic molecules or organic ferromagnets of recent interest.[9-12] This conclusion can be extended to alternant systems containing heteroatoms. Since the last theoretical study of conjugated polymers with polaronic ferromagnetism was reported,[13] evidence for ferromagnetic coupling in poly(*m*-phenyleneoctatetraene)[14] and poly(*m*-aniline)[15] has increased and provides the basis for consideration of a novel type of organic magnetism.

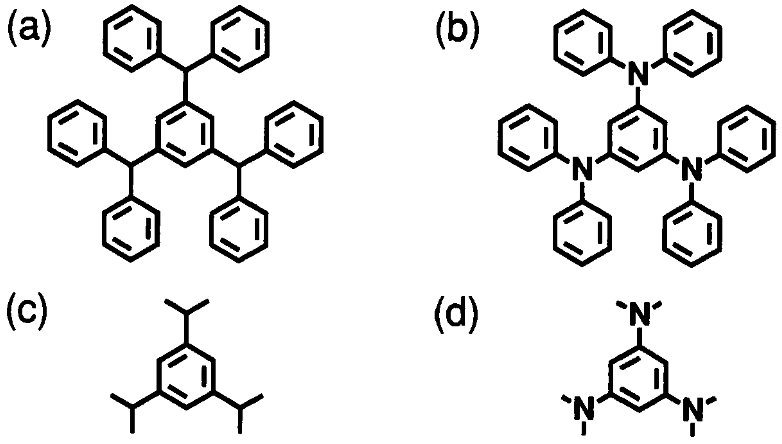

FIGURE 1. Molecular structures of (a) 1,3,5-tris(diphenylmethyl)benzene (TDMB), (b) 1,3,5-tris(diphenylamino)benzene (TDAB), (c) 1,3,5-trimethylene-benzene (TMB), and (d) 1,3,5-triaminobenzene (TAB).

Although there have been a large number of theoretical studies on diradicals,[16-22] detailed calculations on triradical character have not been carried out to our knowledge. In the present paper, our main concern is the electronic structure of this kind of quartet molecules with trigonal symmetry. As seen in Figure 1, the trication of 1,3,5-triaminobenzene (TAB^{3+}) and $TDAB^{3+}$ are isoelectronic systems with 1,3,5-trimethylenebenzene (TMB) and TDMB, respectively. To clarify the electronic structures of such quartet molecules, here we have made an ab initio MO investigation of TMB and

TAB^{3+} in the unrestricted Hartree-Fock (UHF) scheme.# We performed the calculations at both planar and nonplanar geometries in order to provide a chemically useful description of these quartet molecules. Geometries were optimized using the UHF MO method employing the STO-3G minimal basis[23a] after which energies were recalculated with the extended 4-31 G set.[23b] These calculations were performed with the Gaussian 90 program.[24]

ESR OF CATIONIC TRIRADICAL OF TDAB

Let us now summarize the previous ESR study on the cationic triradical of TDAB.[5,6] TDAB was synthesized from 1,3,5-tribromobenzene and diphenylamine using the Ullmann reaction. The cationic triradical of TDAB was easily prepared in an ESR sample tube under nitrogen atmosphere by oxidation of TDAB with trifluoroacetic anhydride in the presence of n-Bu_4NBF_4 in CH_2Cl_2. Although the role of trifluoroacetic anhydride is currently not clear, the charge-transfer reaction between TDAB and n-Bu_4NBF_4 is considered to be activated by this agent. The cationic triradical is orange in color and is stable under vacuum or purified nitrogen at room temperature. However, we have not yet succeeded in isolating the triradical.

In Figure 2, the ESR spectrum of the CH_2Cl_2 solution of the triradical of TDAB frozen into rigid glass at 123 K is shown. The spectrum consists of several $\Delta m_s = \pm 1$ signals and is quite similar to that of the triradical of 1,3,5-tris[(di(biphenyl-4-yl)methyl)]benzene (TDBMB) observed by Brickmann and Kothe.[4] The ESR g-value of the TDAB triradical was determined to be 2.002, thus isotropic and close to the value for a free electron.

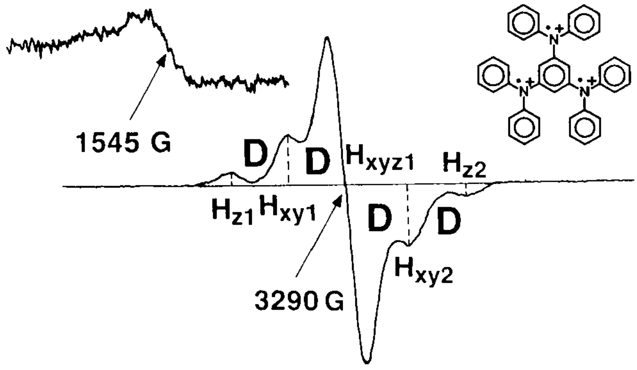

FIGURE 2. ESR spectrum of the cationic triradical of TDAB in CH_2Cl_2 glass at 123 K. H_{z1}, H_{xy1}, H_{xyz1}, H_{xy2}, and H_{z2} are the axial resonance fields. D is a zero-field-splitting parameter. The half-field resonance corresponding to the $\Delta m_s = \pm 2$ transition is observed under 50 K.

The zero-field splitting parameter D was determined to be 13.1 G (0.0012 cm^{-1}) from the difference of H_{z1} and H_{z2}. This value is about one-third of the value of D for TDBMB.[4] This reflects the difference in the spin density distribution between the carbon- and the nitrogen-centered radical species. Assuming the point-dipole approximation in the expression of D, the extent of the spin delocalization for the cationic radical is probably slightly larger than that for the neutral one, likely due to Coulomb repulsion or the presence of heteroatoms. Such diminished interactions of unpaired electrons in a heteroatomic system has been reported by Breslow et al.[25] As shown also in Figure 2, the half-field resonance corresponding to the $\Delta m_s = \pm 2$ transition was detected under 50 K. This clearly indicates that the observed species is in a multiplet state. However, the $\Delta m_s = \pm 3$ transition associated with a three electron flip has not been observed. The intensities of the three transitions $\Delta m_s = \pm 1, \pm 2$, and ± 3 are expected in a ratio of $1 : (D/H)^2 : (D/H)^4$.[26] In this spectrum with $D = 13.1$ G, the intensity of the $\Delta m_s = \pm 3$ transition may be only 10^{-8} relative to that of the $\Delta m_s = \pm 1$ transition. Thus, there are obvious difficulties in detecting the $\Delta m_s = \pm 3$ transition in the ESR spectrum.

The temperature-dependence of the ESR signal intensity indicates whether the observed quartet is the ground state or an excited one. The ESR intensity of the $\Delta m_s = \pm 1$ transition was observed to increase with a decrease in temperature, where the signal intensity obeys the Curie-Weiss law between 15 and 150 K. Therefore either the observed quartet is the ground state or the doublet and quartet are nearly degenerate ground states.

NEARLY THREEFOLD DEGENERATE SYSTEM

Prior to the description of the detailed calculation results, we would like to examine the NBMOs, since in the present article we extensively use the concept of the NBMO although it normally applies to only the Hückel MO approximation dealing with the π-orbital patterns. The three NBMOs of planar TMB belonging to the D_{3h} point group obtained by the zero sum rule[7] based on the Hückel MO approximation are shown in Figure 3, where the two e" MOs are exactly degenerate and, moreover, nearly degenerate with the a_2" MO from the group theoretical considerations.

From inspection of these three NBMOs, the quartet state is expected to energetically lie below the doublet since the NBMOs are nondisjoint: they span common atoms.[27] We consider that the Jahn-Teller distortions[28] of the three methylenes play an important role in the energy determination of the quartet and the doublet. To highlight an interesting aspect of the Jahn-Teller effect, we examine the bond-length distortions and the twisting of these methylene or amino groups.

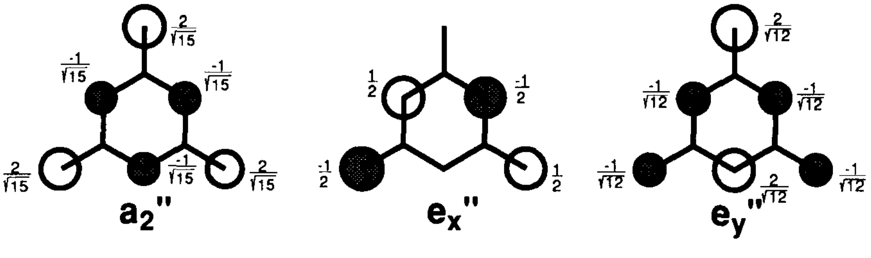

FIGURE 3 Nearly threefold-degenerate nonbonding molecular orbitals (NBMOs) of TMB.

While $^4A_2''$ state probably prefers D_{3h} geometry, the doublet states will not, since in D_{3h} geometry the lowest doublet state should have $^2E''$ symmetry. According to the Jahn-Teller effect, an E state in D_{3h} is subject to the first-order distortions of the molecular geometry which remove the degeneracy. Bond-length distortions conforming to the e' representation of TMB or TAB^{3+} in D_{3h} are the Jahn-Teller active modes. The first component of the degenerate pair of displacements belongs to the a_1 representation in C_{2v}, and the second to the b_2 representation in C_{2v}. The second one tends to destroy C_{2v} geometry and leads to C_s one. As also shown in Figure 3, in the C_{2v} subgroup, the correspondence of orbital symmetry with D_{3h} is expressed by

$$a_2'' \rightarrow b_1, \qquad e_y'' \rightarrow b_1, \qquad e_x'' \rightarrow a_2$$

Since a_2'' and e_y'' MOs correlate with the same b_1 representation in C_{2v}, the two MOs will be mixed in the Hartree-Fock calculations.

RESULTS AND DISCUSSION

It has been found that the quartets of TMB and TAB^{3+} have their minimum energy at D_{3h} geometry with the bond length between the substituents and the phenyl ring $r = 1.425$ and 1.396 Å, respectively, the detail of which is relegated to ref. 29. It has been confirmed that the $^4A_2''$ state lies distinctly below any doublet states as described below.

For each of planar TMB and TAB^{3+}, two stationary points on the potential energy surface for C_{2v} structure have been found in the doublet states. One of such C_{2v} structures has a geometry in which one of the three C-C or C-N bonds connecting the substituents (from now on we will call this bridge bond) is much longer than the other two.[29] In contrast, another C_{2v} structure prefers a geometry in which the two bridge bonds are a little shorter than the other.[29] The diagram between various Jahn-Teller distorted geometries of planar TMB and TAB^{3+} is shown in Figure 4.

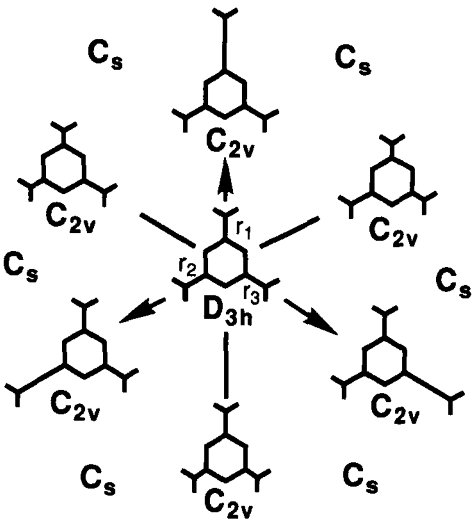

FIGURE 4 Schematic representation of the Jahn-Teller distortion space for planar doublet of TMB and TAB^{3+}.

The center of the figure refers to the parent D_{3h} geometry. Six points on the three arrow-axes correspond to configurations with C_{2v} epikernel symmetry.[30] The distortions in the opposite directions generally do not lead to equivalent configurations. Between any two C_{2v} points in Figure 4, the element of symmetry becomes only the molecular plane. These inbetween points refer to distorted structures conserving the C_s kernel symmetry.[31] However, no stationary points on the potential energy surface for the C_s structure has been found in our MO calculations. The optimized geometries and energies of the doublet states are shown in Table I.

The three NBMOs of $^4A_2''$ state of TMB are nearly degenerate. In $^4A_2''$ state of TAB^{3+}, on the other hand, the energy difference between a_2'' and e'' orbitals are larger than that of TMB. As mentioned above, a_2'' and e_y'' MOs are mixed in the doublet state since they belong to the same b_1 representation in C_{2v}. Note that a_2 in C_{2v} comes from e_x'' MO in D_{3h}, having no relation with a_2'' MO. In TAB^{3+}, the energy level of the a_2 orbital lies well above those of the two occupied b_1 orbitals. Hence, it should be more difficult for $^2A_2$ state to appear in the two planar C_{2v} structures of TAB^{3+}.

Having described the planar geometries, let us now look at the energy change when twisting one methylene or amino group in the planar doublet by 90° around the bridge bond (orthogonal doublet).[29] When one methylene or amino group is twisted out of the plane by 90°, a single twofold rotation and a molecular plane remains, and hence the new point group is also C_{2v}. As also listed in Table I, the orthogonal TMB is less stable than the planar ones.

TABLE I. Optimized doublet geometries and relative energies in TMB and TAB^{3+} at the ab initio UHF level employing 4-31G//STO-3G basis sets.

		r_1	r_2	r_3	energy (kcal/mol)[a]	state[b]
TMB						
	C_{2v}	1.534	1.427	1.427	26.082	$^2A_2$
	C_{2v}	1.427	1.369	1.369	115.856	$^2B_1$
	C_s		not found			
	C_{2v} (twist)	1.506	1.426	1.426	158.506	$^2A_2$
	C_{2v} (twist)[c]	1.506	1.506	1.428	41.242	$^2A_2$
TAB^{3+}						
	C_{2v}	1.521	1.397	1.397	102.726	$^2B_1$
	C_{2v}	1.414	1.347	1.347	85.448	$^2B_1$
	C_s		not found			
	C_{2v} (twist)	1.495	1.344	1.344	16.877	$^2A_1$
	C_{2v} (twist)[c]	1.495	1.495	1.397	45.752	$^2A_2$

[a] Energy relative to the optimized D_{3h} quartet state. TMB: -345.5189 a.u. (r = 1.425 Å), TAB^{3+}: -394.0704 a.u. (r = 1.396 Å).

[b] Strictly speaking, these electronic states are not correct because the UHF wavefunction is not an eigenfunction of the S^2 operator.

[c] Two substituents are twisted by 90° around each bridge bond.

In order to further examine the nonplanar effect, we have calculated the orthogonal structures the two substituents of which are twisted out of the plane by 90°.[29] The point group of the structures still remains in C_{2v}. In this case, TAB^{3+} becomes unstable and, on the other hand, TMB stable. Although the energy gain on the twisting of one amino group is large, the quartet is still predicted to be the ground state of TAB^{3+}. Consequently, the lowest doublet states of TMB and TAB^{3+} are, respectively, $^2A_2$ with the planar geometry where one methylene group has a much longer bridge bond than the other two, and $^2A_1$ with the nonplanar C_{2v} geometry where one amino group is twisted out of the molecular plane by 90°. Thus, the $^4A_2''$ states with the planar D_{3h} geometry are predicted to lie well below these doublet states.

Having described the electronic structures of TMB and TAB^{3+}, we would like to discuss the quartet-doublet splitting energy of $TDAB^{3+}$ using the semiempirical AM1 method. The geometries of the quartet state (D_3) and the Jahn-Teller distorted doublet state (C_2) of $TDAB^{3+}$ are shown in Fig. 5. In the quartet state, the three dihedral angles between the central benzene and the nitrogens are 34.4°, and those between the nitrogens and the peripheral benzenes are 33.7°. On the other hand, in the doublet state, one dihedral angle between the central benzene and the nitrogen is nearly 90°. The quartet state of TDAB^{3+} is predicted to lie slightly below the doublet state by 0.89 kcal /mol, being consistent with the ESR measurement.

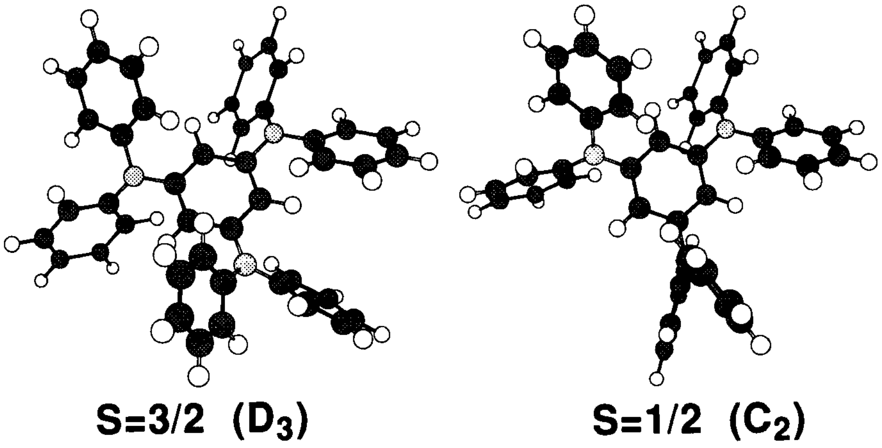

FIGURE 5 Molecular structures of the quartet state with the D_3 geometry (Left) and the doublet state with the C_2 geometry (Right).

CONCLUSION

The observed ESR spectrum of the cationic radicals, which are rigidly held but randomly oriented with respect to the magnetic field in CH_2Cl_2 glass, agreed well with the theoretical prediction for a quartet spin state. The temperature-dependence of the intensity for $\Delta m_S = \pm 1$ transition confirmed that the quartet is the ground state. This material is therefore of interest as an example of a novel type of organic magnetism. The stability of this radical is probably attributable to the presence of heteroatoms in the π-conjugation as seen in the 1,1'-diphenyl-2-picrylhydrazyl (DPPH) radical. A particularly unique feature of TDAB is that the observed intramolecular ferromagnetic interaction operates among the cationic radicals. The present ferromagnetic interaction might provide important information about the still unknown chemical nature of the organic ferromagnetic material, poly(1,3,5-triaminobenzene).[32]

Moreover, we have investigated the electronic structures of non-Kekulé isoelectronic systems TMB, TAB^{3+}, and TDAB^{3+} by means of the MO method within the UHF scheme. Three types of conclusions can be drawn from this MO study. The first of these is on the electronic ground state of TMB and TAB^{3+}. In both of these, the quartet state with the planar D_{3h} geometry is predicted to lie well below any doublet states. Also, the quartet state of $TDAB^{3+}$ with a threefold axis (D_3 geometry) lies slightly below the Jahn-Teller distorted doublet state.

The second conclusion regards the lowest doublet state of these molecules. The molecular shape of the lowest doublet for TMB is the planar C_{2v} geometry in which one methylene has a much longer C-C bridge bond than the other two. On the other hand, the lowest doublet state for TAB^{3+} prefers the orthogonal geometry in which one amino group is twisted out of the molecular plane.

Finally the quartet ground state of this type of non-Kekulé molecules results from the nearly threefold-degenerate NBMOs. Our calculations are fully consistent with the previous experimental studies of this type of triradicals.[1-6] Moreover, the simple rules for predicting a spin alignment based on the valence bond[8] and the MO[27] theories have been confirmed to provide a powerful guide for the molecular design of high-spin molecules and organic ferromagnets.

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Usually, the spin-contamination for doublet and quartet states of conjugated π systems is very large in the UHF method since the UHF wavefunction is not an eigenfunction of the S^2 operator. In the present calculations, the $<S^2>$ values for the doublet and quartet states are 0.98~2.57 and 4.4~4.5, respectively, due to the spin-polarization effect of a benzene ring. The spin-projection technique could not improve the wavefunctions in some cases.

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