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Jiro Abe, Tomoo Miyazaki, and Hiroaki Takahashi

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***Ab initio* molecular orbital and resonance Raman studies of the structure of the lowest triplet state of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine**

Jiro Abe, Tomo-o Miyazaki, and Hiroaki Takahashi

Department of Chemistry, School of Science and Engineering, Waseda University, Tokyo 160, Japan

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Ab initio STO-3G and semiempirical modified neglect of diatomic overlap (MNDO) calculations have been performed for the ground state, the radical cation, and the lowest triplet state of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD). The geometry of each state optimized by the *ab initio* calculation is not much different from that optimized by the MNDO calculation. The optimized structures of the ground state and the radical cation are both in good agreement with the structures determined by x-ray diffraction. It is concluded based on the molecular-orbital calculations as well as on our previously reported time-resolved resonance Raman spectra that the lowest triplet state of TMPD takes a "softened" 1,4-quinoid-like structure in the planar configuration with the C=C bonds of the phenyl ring being lengthened while the N-Ph bonds shortened.

I. INTRODUCTION

In a previous paper,¹ we have shown by time-resolved resonance Raman spectroscopy that the frequency shifts on isotopic substitutions of the lowest triplet state of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) are anomalous in that the Raman band at 1530 cm^{-1} which is considered to be attributable to the $8a$ mode (Wilson vibration number²) of the phenyl group is shifted not only on the phenyl deuteration but also on the methyl deuteration or the ^{15}N substitution. This is in sharp contrast to the $8a$ mode of the ground state or the radical cation which does not exhibit appreciable shifting on the methyl deuteration or the ^{15}N substitution.

We have interpreted the frequency shifts of the band at 1530 cm^{-1} as being due to coupling of the phenyl $8a$ mode with the N-Ph symmetric stretch caused by weakening of the C=C bonds of the phenyl ring accompanied by strengthening of the N-Ph bonds in the lowest triplet state.

Poizat *et al.*³ also reported the anomalous frequency shift of this band on the methyl deuteration. However, they considered that the triplet state of TMPD takes a boat-shaped structure with double-bond character of the N-Ph bonds which constitute the chromophore. Since the phenyl $8a$ mode would no longer be resonance enhanced with this configuration, the Raman band at 1533 cm^{-1} was attributed to the N-Ph symmetric stretch.

This molecular-orbital (MO) study was undertaken in order to investigate which of the two proposed structures and hence the explanations about the anomalous frequency shifts of the band at 1530 cm^{-1} is appropriate for the triplet state of TMPD.

II. MO CALCULATIONS

Since the structures of the ground state and the radical cation were determined by x-ray diffraction,^{4,5} not only the triplet state but also these two states were calculated in order to check the applicability of the MO calculations to TMPD.

Semiempirical molecular-orbital calculations were carried out using the standard modified neglect of diatomic overlap (MNDO) method⁶ with the parameters implemen-

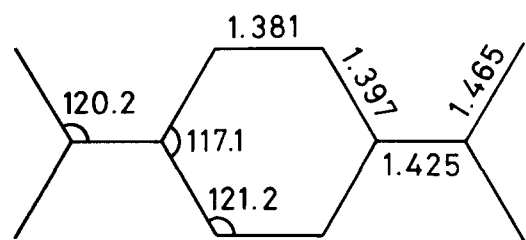
ted in the program package AMPAC.⁷ The RHF (spin-restricted Hartree-Fock) version was used for the ground state and the UHF (spin-unrestricted Hartree-Fock) version for the radical cation. For the triplet state, the RHF version was employed combining with the CI (configuration interaction) treatment which involves 3×3 CI matrices. All the geometries of the ground state, the triplet state, and the radical cation were fully optimized using the DFP (Davidon-Fletcher-Powell) algorithm⁸ incorporated in the program AMPAC without making any assumptions.

The program GAUSSIAN 82 (Ref. 9) was used for the *ab initio* calculations. The geometry optimization was performed using the RHF/STO-3G approximation for the ground state and the UHF/STO-3G approximation for the radical cation and the triplet state. All geometry optimizations were carried out with the restriction in which the molecule maintains at least the twofold symmetry axis perpendicular to the phenyl ring.

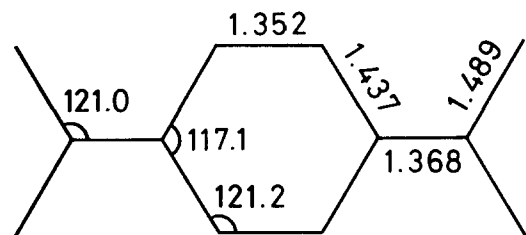
III. RESULTS AND DISCUSSION

The results of the *ab initio* calculations of optimized structural parameters (bond lengths and angles) of the ground state, the triplet state, and the radical cation of TMPD are given in Fig. 1 and both *ab initio* and MNDO results of the optimized bond lengths of the molecular framework and the bond orders obtained by the MNDO calculation are listed in Table I along with the observed bond lengths of the ground state and the radical cation.

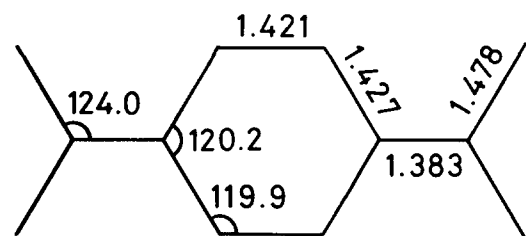
The agreement between the calculated and observed bond lengths of the ground state and the radical cation is more than satisfactory. The very good agreement of the *ab initio* results with observed values for the ground state, however, might be fortuitous when it is considered that the observed values were obtained for the solid state by x-ray diffraction^{4,5} while the calculated values apply to the gaseous state. Although the *ab initio* and MNDO results are not much different from each other, the former appears to give slightly better agreement with the observed values than the latter as is commonly believed. The good agreement between



(A) ground state



(B) radical cation



(C) triplet state

FIG. 1 Optimized geometry of the ground state, the radical cation and the triplet state: (A) ground state; (B) radical cation; (C) triplet state. The bond lengths and angles related to hydrogen atoms are not given here.

TABLE I. Optimized geometry of the ground state, the radical cation, and the triplet state calculated by *ab initio* and MNDO methods. The value in parentheses represents the bond order obtained by the MNDO method.

		Bond length (Å)		
		C ¹ -C ²	C ² -C ³	C ¹ -N
Ground state	Observed (Ref. 4)	1.397	1.390	1.414
	<i>Ab initio</i>	1.397	1.381	1.425
	MNDO-RHF	1.416	1.405	1.438
		(1.38)	(1.42)	(0.96)
Radical cation	Observed (Ref. 5)	1.415	1.361	1.355
	<i>Ab initio</i>	1.437	1.352	1.368
	MNDO-UHF	1.453	1.379	1.372
		(1.14)	(1.63)	(1.27)
Triplet state	<i>Ab initio</i>	1.427	1.421	1.383
	MNDO-CI	1.441	1.412	1.391
		(1.18)	(1.24)	(1.15)

the calculated and observed geometries indicates that both STO-3G and MNDO approximations can be considered to be sufficiently accurate even for a large molecule like TMPD at least for the ground state and the radical cation. We see that the radical cation takes a quinoid structure.

Since observed values of the structural parameters are not available for the lowest triplet state, it is not possible to know with certainty the degree of reliability of the MO calculations. Generally, the wave functions are believed to be more diffuse or delocalized in the excited states than in the ground state. Therefore, it may be argued that for the lowest triplet state, a 4-31G or 4-31G* approximation with CI treatment is needed to obtain reliable geometries instead of a simple STO-3G approximation.

Indeed, we have calculated the ionization energy of TMPD by use of STO-3G, 4-31G, and 4-31G* approximations applying Koopmans theorem and obtained 4.6, 6.4, and 6.4 eV, respectively. Since the observed value in the gaseous state is 6.6 eV, the superiority of the 4-31G and 4-31G* approximations over the STO-3G approximation is evident. However, since both 4-31G and 4-31G* approximations involve too much computation, it is not practical to apply them to a large molecule like TMPD for obtaining the optimized structure in regard to computation time and cost. Because of the fact that both STO-3G and MNDO-CI approximations give nearly the same geometry and that, as will be discussed later, the isotopic frequency shifts of the band at 1530 cm⁻¹ of the triplet state suggest the same geometry as the calculated one, we believe that the simple STO-3G and MNDO-CI approximations adopted in the present study can qualitatively be relied upon also for the lowest triplet state, if not quantitatively.

In order not to fall into the local energy minimum, the geometry optimizations were performed with various kinds of initial structures including nonplanar configurations of the skeleton. However, all three states obtained by use of the *ab initio* SZ (single zeta) self-consistent-field level approximation gave the energy minima for the structures having *D*_{2h} symmetry. Thus, the boat-shaped configuration proposed by Poizat *et al.*³ can definitely be ruled out for the structure of the triplet state.

Table II compares the frequency shifts on isotopic substitutions of the band at 1530 cm⁻¹ of the lowest triplet state with those of the phenyl 8a mode and the N-Ph symmetric stretch of the ground state and the radical cation. It is readily recognized that the band at 1530 cm⁻¹ of the lowest triplet state behaves quite differently with respect to the isotopic substitutions both from the phenyl 8a mode and the N-Ph symmetric stretch of the ground state or the radical cation.

The observation that the band at 1530 cm⁻¹ of the triplet state exhibits large shifts not only on the phenyl deuteration but also on the methyl deuteration and on the ¹⁵N substitution indicates that this band can be attributed neither to the phenyl 8a mode nor to the N-Ph symmetric stretch; the 8a mode is expected to shift exclusively on the phenyl deuteration, whereas the N-Ph symmetric stretch on the methyl deuteration or on the ¹⁵N substitution.

The isotopic frequency shifts show that the vibrational mode corresponding to the 1530 cm⁻¹ band is neither local-

TABLE II. Comparisons of the frequency shifts on isotopic substitutions of the 1530 cm^{-1} band of the triplet state with those of the phenyl $8a$ mode and the N-Ph symmetric stretch of the ground state and the radical cation.

Mode	Frequency (cm^{-1}) TMPD	Frequency shifts (cm^{-1})		
		TMPD- d_4	TMPD- $^{15}\text{N}_2$	TMPD- d_{12}
Triplet state	1530	-14	-13	-17
Ground state	$8a$	-24	0	0
	N-Ph sym. str.	-3	-13	-13
Radical cation	$8a$	-27	-2	-3
	N-Ph sym. str.	0	-9	-43

ized to the phenyl ring nor to the N-Ph bonds and suggest that the concept of "group vibrations," such as the phenyl $8a$ mode or the N-Ph stretch, are not applicable in the strict sense to the lowest triplet state. Since in the lowest triplet state an electron is elevated to an antibonding orbital, the phenyl ring must lose its rigidity and becomes "softened" and when the bond orders of the C=C bonds of the phenyl ring and the N-Ph bonds are not much different from each other, a strong coupling between the phenyl $8a$ mode and the N-Ph symmetric stretch is expected to occur. The observation that the band at 1530 cm^{-1} of the lowest triplet state is downshifted almost the same amount of about 15 cm^{-1} on the phenyl deuteration, the ^{15}N substitution and the methyl deuteration is indicative of a strong coupling between the phenyl $8a$ mode and the N-Ph symmetric stretch and points to the "softened" structure in which the bond orders of the C=C bonds of the phenyl ring and the N-Ph bonds are approximately the same.

In the optimized structure of the lowest triplet state shown in Fig. 1 and summarized in Table I, we see that the C=C bonds of the phenyl ring are lengthened while the N-Ph bonds are shortened compared to those of the ground state to an extent that the bond orders of both C=C and N-Ph bonds adopt approximately the same value of 1.2. This structure of the lowest triplet state agrees quite well with that predicted from the isotopic frequency shifts of the resonance Raman spectra of the lowest triplet state.

Based on the geometry optimization by the *ab initio* and MNDO calculations and on the isotopic frequency shifts of the resonance Raman spectra, we conclude that the lowest

triplet state of TMPD takes a planar structure in which the C=C bonds of the phenyl ring is lengthened and the N-Ph bonds shortened to an extent that all bonds take almost the same bond order. Since the $\text{C}^2=\text{C}^3$ bonds are calculated to be slightly shorter than the $\text{C}^1=\text{C}^2$ bonds, particularly by use of the MNDO-CI approximation, this structure may be termed "softened" 1,4-quinoid-like structure.

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