

High-Spin Stability of Triiminiummethane Ion A Comparative Study with Trimethylenemethane

Masashi HATANAKA* and Ryuichi SHIBA

Department of Materials Science and Engineering, Graduate School of Engineering, Tokyo Denki University
2-2 Kanda-Nishiki-cho, Chiyoda-ku, Tokyo, 101-8457, Japan

*e-mail: mhatanaka@xug.biglobe.ne.jp

(Received: January 12, 2006; Accepted for publication: March 24, 2006; Published on Web: July 18, 2006)

High-spin stability of non-Kekulé-type molecule triiminiummethane ion (TIM^{3+}) is discussed using the semiempirical molecular orbital method. The triplet ground state $^3A_2'$ with a D_{3h} geometry is predicted to lie below the Jahn-Teller distorted singlet states similar to trimethylenemethane (TMM). The lowest singlet states 1B_1 , 1B_2 and 1A_1 with C_{2v} geometries are nearly degenerate. The spin-density distribution of the $^3A_2'$ state is calculated and the origin of the spin alignment is discussed relating to the spin-polarization rule characteristic of high-spin organic molecules. The valence bond analysis on the spin states of TIM^{3+} is also carried out.

Keywords: Non-Kekule-type molecules, Molecular orbital method, High-spin organic molecules, Spin density, Triiminiummethane ion

1 Introduction

High-spin organic molecules are very well-designed materials employing quantum chemistry. The simplest high-spin organic molecule is trimethylenemethane (TMM : Figure 1(a)). This is a typical non-Kekulé-type molecule. As a zeroth-order theoretical analysis, triplet ground state is predicted by the Hund's rule because TMM has twofold-degenerate NBMO (non-bonding molecular orbital)s and two unpaired electrons [1].

Dowd synthesized TMM and observed its ESR spectrum in a frozen matrix [2]. A recent photoelectron spectroscopic study on TMM radical anion reports the direct determination of the singlet-triplet energy splitting [3]. Thus the triplet ground state of TMM has been established both theoretically and experimentally. The essential origin of the high-spin state is twofold-degenerate NBMOs.

Since Mataga [4] and Ovchinnikov [5] suggested the possibility of organic ferromagnets based on MO (Molecular Orbital) and VB (Valence Bond) method, respectively, many high-spin hydrocarbons have been synthesized [6, 7]. High-spin states often have been found in heteroatom-containing systems and their stabilities have been established by molecular orbital studies [8–10]. In particular, there has been increasing interest in nitrogen-

centered radicals such as aminium radicals because they can be isolated as cationic radical salts in solid states. Recent studies on magnetic properties of aminium radicals are aimed to realize not only high-spin organic molecules but also organic ferromagnets [11–14].

In our previous work [14], we designed polyguanide- and polyuret-based ferromagnets taking account of the non-Kekulé character of nitrogen-centered radicals. In this paper we investigate the spin states of non-Kekulé-type molecule triiminiummethane ion (TIM^{3+} : Figure 1(b)) as an analogue of TMM. It is worthwhile to study the spin states of TIM^{3+} in detail because TIM^{3+} is the simplest nitrogen-centered biradical.

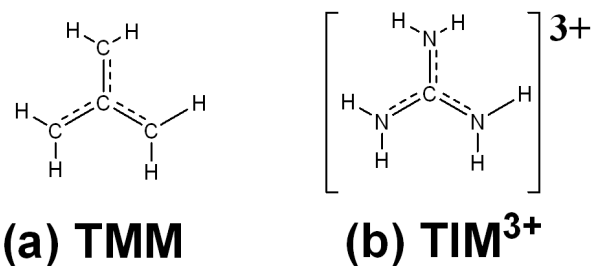


Figure 1. Molecular structures (a) TMM and (b) TIM^{3+} . The resonance structures represent the non-Kekulé character of these molecules.

TIM³⁺ is also predicted to have a triplet ground state intuitively because this molecule is isoelectronic with TMM and has two degenerate SOMO (Single Occupied Molecular Orbital)s due to the threefold axis of symmetry. Theoretical investigation is, however, necessary to establish the high-spin stability of this molecule because the degeneracy of singlet states of TIM³⁺ is lifted by the Jahn-Teller theorem [15].

In order to clarify the spin states of TIM³⁺, the optimized geometries and the relative energies of low-lying electronic states of TIM³⁺ are calculated using semiempirical MO method. The origin of the spin alignment in the triplet TIM³⁺ is also discussed relating to the spin-polarization rule. Furthermore, VB analysis on the ground state of TIM³⁺ is carried out using the resonance structures and the charge distributions.

2 Computational details

Before detailed computations, it is wise to understand the origin of the high-spin stability of TIM³⁺ within a framework of the Hückel MO method.

Because TIM³⁺ is isoelectronic with TMM, we can expect the triplet ground state of TIM³⁺. TMM has twofold-degenerate NBMOs. The shapes of the NBMOs of planar TMM and the symmetry classifications are given in Figure 2. The coefficients of these NBMOs are obtained using NBMO method [16]. The NBMOs are *nondisjoint*; they span common atoms [1].

While the triplet state probably prefers D_{3h} geometry, the closed-shell singlet states are subject to the Jahn-Teller distortion [15] to prefer C_{2v} geometry. The double occupation of one of the two degenerate NBMOs leads to a closed-shell singlet state with a planar C_{2v} geometry. In addition, a 90° rotation of one methylene group leads to a low-energy singlet state with a C_{2v} geometry [17]. The rotation of one methylene group transforms the e''y (b₁) orbital to the b₂ orbital with C_{2v} symmetry. The e''x (a₂) orbital is invariable by the rotation.

The zeroth-order approximate wavefunctions of the energetically low-lying states created by the frontier two electrons are also shown in Figure 2. These wavefunctions satisfy the spin symmetries.

We note that the wavefunctions of the ³A₂', ¹B₁ and ¹B₂ are open-shell type. Although two ¹A₁ states arise from the linear combination of the closed-shell configurations, we direct our attention to the lowest ¹A₁ state. The actual calculations tell us that the antisymmetric combination (having minus sign) approximately describes the lowest ¹A₁ state.

In the actual computations, we employed semiempirical MO method PM3 [18] because our main interest is qualitative high-spin stability of TIM³⁺. PM3 method is very useful for the design of high-spin organic molecules

[10, 14] and gives intuitive and essential description of high-spin states.

Considering the basic perspective as mentioned above, we calculated the optimized geometries and the relative energies of low-lying electronic states of TIM³⁺ in detail using PM3 method. We also calculated the low-lying electronic states of TMM using the same method to compare the magnitude of the high-spin stability.

In order to obtain the optimized geometries and the relative energies we employed CI (Configuration Interaction) method because the electronic states are degenerate. The reference configurations were created by ROHF (Restricted Open-Shell Hartree-Fock) wavefunctions and the active spaces were spanned by four π-orbitals including two NBMOs. The geometrical optimizations were carried out under constraints of D_{3h} symmetry for triplet and C_{2v} symmetry for singlet states. We also obtained the spin distributions by UHF (Unrestricted Hartree Fock) method under the geometries at the PM3-CI level of theory. The calculations were carried out using semiempirical MO program MOPAC 2000 [19].

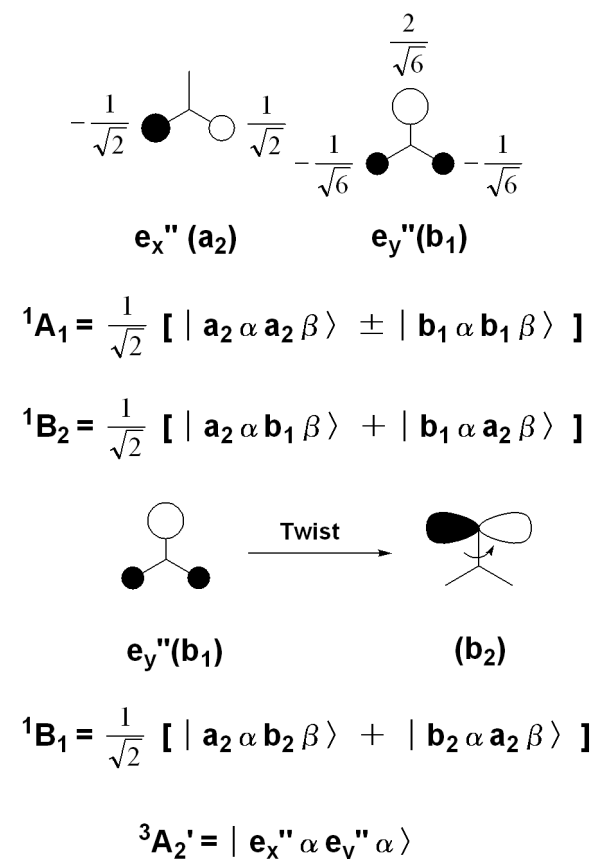


Figure 2. Schematic non-bonding molecular orbitals (NBMOs) of TMM and possible wavefunctions created by frontier two electrons. The symmetry classifications are given for D_{3h} (C_{2v}) point group.

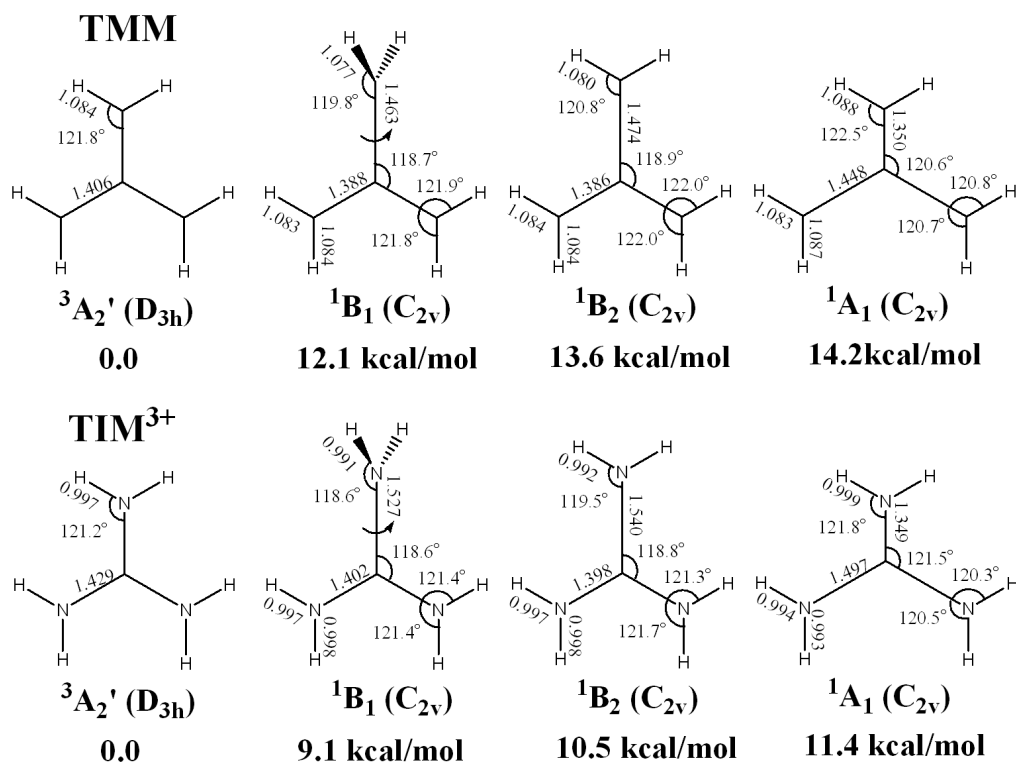


Figure 3. Optimized geometries and relative energies of TMM and TIM³⁺ at the PM3-CI level of theory.

3 Results and Discussions

The optimized geometries and relative energies for the lowest-lying states of TMM and TIM³⁺ at the PM3-CI level of theory are summarized in Figure 3. In TMM the triplet ground state ${}^3A_2'$ with a D_{3h} geometry was predicted to lie below any singlet state. The singlet states 1B_1 , 1B_2 and 1A_1 were nearly degenerate. The 1B_1 state was predicted to have a C_{2v} geometry in which one of the methylene groups was twisted. The 1B_2 state with an open-shell configuration was predicted to have a planar C_{2v} geometry in which one of the C-C bonds is longer than those of the other two. In contrast to the 1B_2 state, the 1A_1 state with a closed-shell configuration was predicted to have a planar C_{2v} geometry in which one of the C-C bonds was shorter than those of the other two. These geometries obtained by PM3-CI calculations are qualitatively consistent with recent ab initio studies [17, 21].

We direct our attention to the singlet-triplet energy splittings of planar TMM because photoelectron spectroscopy of TMM anion radical has determined the 1A_1 - ${}^3A_2'$ energy splitting to be 16.1 ± 0.1 kcal/mol [3]. Our calculation estimated the 1A_1 - ${}^3A_2'$ energy splitting to be 14.2 kcal/mol. This value is close enough to the experimental result. Recent ab initio studies also have predicted that the lowest planar singlet state is Jahn-Teller distorted

1A_1 and the twisted 1B_1 state lies 0–6 kcal/mol below the 1A_1 state [3, 17]. We feel that PM3-CI calculation is sufficient for not only qualitative but also quantitative estimation of the high-spin stabilities. Our main interest is, however, the qualitative description of high-spin stability of TIM³⁺ as an analogy of TMM, as emphasized above.

Let us consider the spin states of TIM³⁺. The triplet ground state ${}^3A_2'$ with a D_{3h} geometry was predicted to lie below any singlet state similar to TMM. The singlet states 1B_1 , 1B_2 and 1A_1 were nearly degenerate. The lowest singlet state was predicted to be 1B_1 and have a C_{2v} geometry in which one of the amino groups was twisted. This state was predicted to lie 9.1 kcal/mol above the ${}^3A_2'$ state. The 1B_2 state with an open-shell configuration was predicted to have a planar C_{2v} geometry in which one of the C-N bonds was longer than those of the other two. In contrast to the 1B_2 state, the 1A_1 state with a closed-shell configuration was predicted to have a planar C_{2v} geometry in which one of the C-N bonds was shorter than those of the other two. The singlet-triplet splitting energies were about 3 kcal/mol lower than those of TMM.

According to Ovchinnikov's paper [5], any conjugated system is described within a framework of the VB theory and the spin state is analyzed using the Heisenberg Hamiltonian (Equation 1), where J_{ij} is the exchange in-

tegral ($J_{ij} > 0$), S_i is the spin operator of the atom with subscript i . Summation includes the nearest neighbors.

$$H = \sum_{i,j} J_{ij} \left(S_i S_j - \frac{1}{4} \right) \quad (1)$$

The expectation value of this Hamiltonian is minimized when all localized spins have opposite direction. Such an alternation of spins is called 'spin polarization' [20]. Therefore, it is worthwhile to calculate the spin distribution of TIM^{3+} and to compare it with that of TMM. It is impossible to calculate minus spin densities by the CI method because the reference configurations are based on ROHF wavefunctions. The UHF method is, however, very suitable for this purpose. Although the UHF wavefunctions are not exactly the eigenfunctions of the spin-squared operator $\langle S^2 \rangle$, it is very useful in describing intuitive spin distributions with plus and minus signs. In view of the spin polarization, UHF wavefunctions resemble VB wavefunctions.

The π -spin densities coming from the $2p_z$ atomic orbitals of the triplet TMM and TIM^{3+} are shown in Figure 4(a) and (b), respectively. $\langle S^2 \rangle$ values are also shown. We

think that our UHF calculations well describe the triplet states because $\langle S^2 \rangle$ values are very close to 2. Both TMM and TIM^{3+} showed strong spin polarizations. The central spins have minus sign and peripheral spins have plus sign. It is interesting that the spin distribution of TIM^{3+} quite resembles that of TMM.

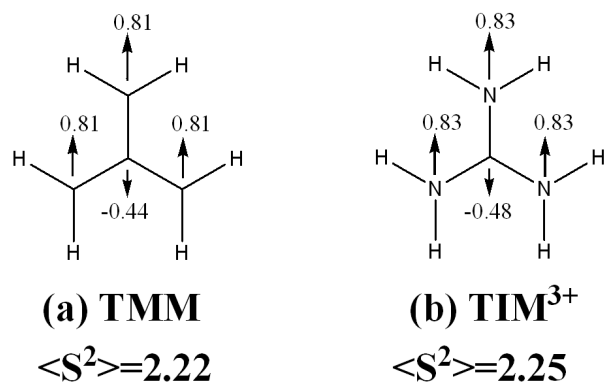


Figure 4. π -spin densities of the triplet states of (a) TMM and (b) TIM^{3+} at the PM3-UHF//PM3-CI level of theory. $\langle S^2 \rangle$ is the spin-squared expectation value.

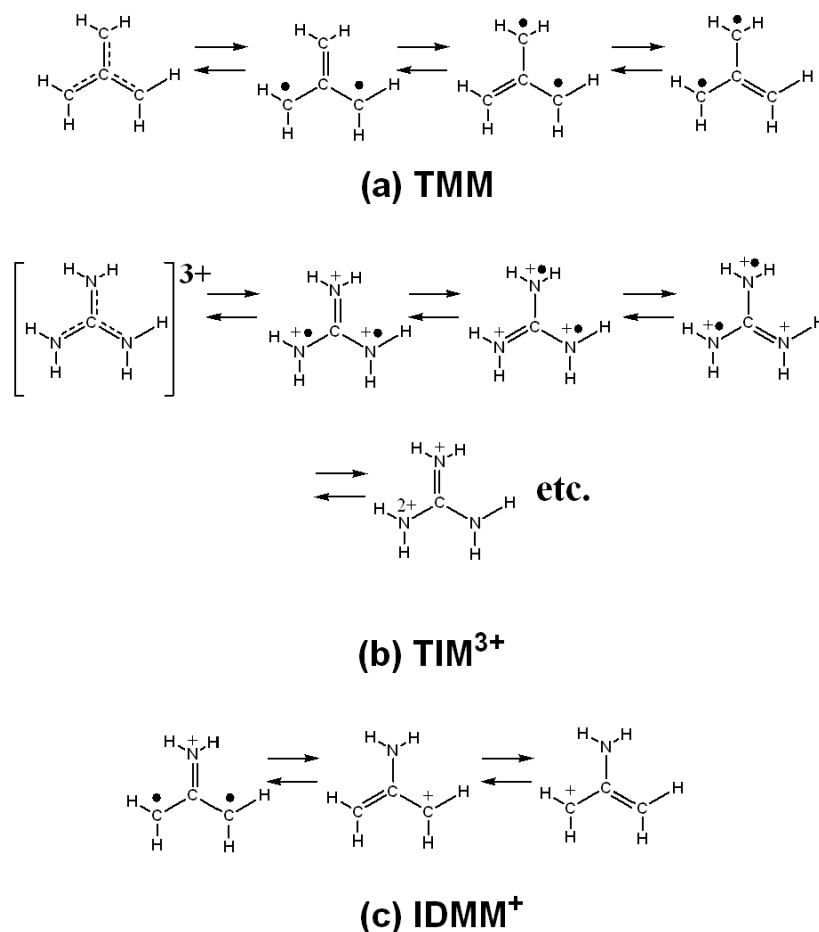


Figure 5. Resonance structures of (a) TMM, (b) TIM^{3+} and (c) $IDMM^+$.

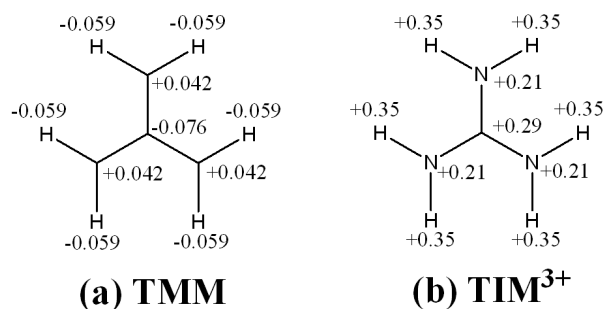


Figure 6. Charge distributions of (a) TMM and (b) TIM^{3+} at the PM3-UHF//PM3-CI level of theory.

The VB analysis using resonance structures is perhaps most intuitive to explain this situation. Figure 5 shows the resonance structures of TMM (Figure 5(a)), TIM^{3+} (Figure 5(b)) and iminiumdimethylenemethane ion (IDMM^+ ; Figure 5(c)) which is a mono-aza analog of TMM. TMM and TIM^{3+} are isoelectronic and their ground states are described in the left hand side of Figure 5(a) and (b) with D_{3h} geometries and no bond alternation. These resonance structures are consistent with the calculated geometries. We can expect their triplet ground states from the resonance structures containing three biradical contributions described in Figure 5(a) and (b). In TIM^{3+} the spin-paired structure is very unstable because the formal charge of one of the nitrogen atoms is +2 (Figure 5(b)). The main contributor is described not by one resonance structure but by three equivalent biradical structures. Thus the essential character of TIM^{3+} seems to be well described by the most left hand side in Figure 5(b) in which positive charges are delocalized on not only the nitrogen atoms and but also the carbon atom.

Interestingly, IDMM^+ is predicted to have a singlet ground state [21]. This is explained using resonance structures in the right-most hand in Figure 5(c). The spin-paired structures in which the positive charge is localized on carbon atoms are more stable than that of the biradical structure in the left hand side because the electronegativity of the nitrogen atom is higher than that of the carbon atoms. The summed group charges of the ground state of IDMM^+ are reported in [21]; amino group; +0.05, central carbon; +0.15, methylene group; +0.40. Thus the ground state of IDMM^+ is expected to be singlet. Although TIM^{3+} is a tri-aza analogue of TMM, we can expect the triplet ground state because the spin-paired structures are very unstable as mentioned above.

In order to confirm the VB analysis as described above, we calculated the net atomic charges of TMM and TIM^{3+} using the UHF method under the geometries at the PM3-CI level of theory. The charge distributions of triplet TMM and TIM^{3+} obtained by the UHF calculations are shown in Figure 6(a) and (b), respectively. In TMM the net atomic charge is almost zero. On the other

hand, the net atomic charge of TIM^{3+} is delocalized on all atoms. The central carbon is also positively charged as well as the nitrogen atoms. This is consistent with the qualitative analysis as mentioned above.

4 Conclusions

We have investigated the high-spin stability of non-Kekulé-type molecules triiminiummethane ion (TIM^{3+}) using the semiempirical molecular orbital methods. The triplet ground state $^3A_2'$ with a D_{3h} geometry was predicted to lie below the Jahn-Teller distorted singlet states similar to trimethylenemethane (TMM). The lowest singlet states 1B_1 , 1B_2 and 1A_1 states were nearly degenerate. The 1B_1 state was predicted to have a C_{2v} geometry in which one of the amino groups was twisted. The 1B_2 state with an open-shell configuration was predicted to have a planar C_{2v} geometry in which one of the C-N bonds was longer than those of the other two. In contrast to the 1B_2 state, the 1A_1 state with a closed-shell configuration was predicted to have a planar C_{2v} geometry in which one of the C-N bonds was shorter than those of the other two. The spin-density distribution of the $^3A_2'$ state was also calculated and discussed relating to the spin-polarization rule. The origin of the high-spin preference was attributed to the resonance structure in which the positive charges are delocalized on the nitrogen and carbon atoms.

References

- [1] W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, **99**, 4587 (1977).
- [2] P. Dowd, *Acc. Chem. Res.*, **5**, 242 (1972).
- [3] P. G. Wenthold, J. Hu, R. R. Squires, W. C. Lineberger, *J. Am. Chem. Soc.*, **118**, 475 (1996).
- [4] N. Mataga, *Theor. Chim. Acta*, **10**, 372 (1968).
- [5] A. A. Ovchinnikov, *Theor. Chim. Acta*, **47**, 297 (1978).
- [6] H. Iwamura, *Adv. Phys. Org. Chem.*, **26**, 179 (1990).
- [7] A. Rajca, *Chem. Rev.*, **94**, 871 (1994).
- [8] K. Yoshizawa, M. Hatanaka, A. Ito, K. Tanaka and T. Yamabe, *Mol. Cryst. Liq. Cryst.*, **232**, 323 (1993).
- [9] K. Yoshizawa, M. Hatanaka, Y. Matsuzaki, K. Tanaka and T. Yamabe, *J. Chem. Phys.*, **100**, 4453 (1994).
- [10] K. Yoshizawa, T. Kuga, T. Sato, M. Hatanaka, K. Tanaka and T. Yamabe, *Bull. Chem. Soc. Jpn.*, **69**, 3443 (1996).

- [11] K. Yoshizawa, M. Hatanaka, H. Ago, K. Tanaka and T. Yamabe, *Bull. Chem. Soc. Jpn.*, **69**, 1417 (1996).
- [12] H. Murata, M. Takahashi, K. Namba, N. Takahashi, and H. Nishide, *J. Org. Chem.*, **69**, 631 (2004).
- [13] H. Murata, D. Miyajima, R. Takada and H. Nishide, *Polym. J.*, **37**, 818 (2005).
- [14] M. Hatanaka and R. Shiba, *J. Comput. Chem. Jpn.*, **4**, 101 (2005).
- [15] H. A. Jahn and E. Teller, *Proc. Roy. Soc. London, Ser. A*, **161**, 220 (1937).
- [16] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).
- [17] C. J. Cramer and B. A. Smith, *J. Phys. Chem.*, **100**, 9664 (1996).
- [18] J. J. P. Stewart, *J. Comp. Chem.*, **10**, 209 (1989).
- [19] J. J. P. Stewart, *MOPAC 2000 in Chem3D*, Ultra version 8.0, CambridgeSoft.
- [20] K. Yamaguchi, Y. Toyoda and T. Fueno, *Synth. Met.*, **19**, 81 (1987).
- [21] J. Li, S. E. Worthington and C. J. Cramer, *J. Chem. Soc., Perkin Trans. 2*, **1998**, 1045.