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Electronic Structure of Methylacetylene Radical Anion: An EPR and MO Study†

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An EPR and MO study has been carried out to elucidate the electronic structure of methylacetylene (MA) radical anion generated in glassy 2-methyltetrahydrofuran matrix by ionization radiation at 77 K. The EPR spectrum was dominated by a large and slightly anisotropic ^{1}H hf splitting of ca. 4.53 mT due to one ethynyl proton. With the help of a selectively deuteriated methylacetylene, MA-d_3, the anisotropic hf and g-values were determined: the principal hf ($\tilde{A}$) and $\tilde{g}$ values are $A_{xx}=5.36$ mT, $A_{yy}=4.39$ mT, $A_{zz}=3.85$ mT for the ethynyl proton, $a=0.50$ mT for the methyl protons, and $g_{xx}=2.0005$, $g_{yy}=2.0020$, $g_{zz}=2.0021$, respectively. From a comparison of the experimental values with the theoretical ones calculated by *ab initio* MO and INDO methods, a *trans*-bent structure was concluded for MA^-. The formation of MA^- was also confirmed by an electron absorption spectroscopic study.

Electronic structures and reactions of organic radical ions have received much attention from many researchers[1,2] since they are intermediate species formed by one-electron reduction and oxidation reactions and their structural nature may play important roles for the following chemical reactions. Acetylene, one of the simplest hydrocarbons, has a linear structure in the ground state and is expected to have a *trans*-bent structure in its electronically excited states.[3,4] Theoretical calculations have predicted that the acetylene radical anion has a *trans*-structure, but the energy difference between the *trans* and *cis* is as small as 7.4 kcal mol^{-1}.[5] Muto and his collaborators first reported the acetylene radical anion trapped in a 3-methylpentane matrix at 77 K. Consistent with the theoretical prediction, the *trans*-bent structure was concluded based on the EPR data.[6] On the other hand Manceron and Andrews have reported an IR study on an Li–acetylene complex anion radical generated in an Ar matrix and found that the acetylene moiety has a *cis*-bent structure.[7] Kasai has observed the EPR spectrum of the same complex anion and confirmed the *cis*-bent structure.[8] We have recently studied electronic structures of the anion radicals of a series of diethynylsilanes.[9] The unpaired electron was found to be localized mainly on the C≡C triple bond so as to give a large ethynyl proton hf splitting: for example, ca. 5.7 mT for tetraethyldiethynyldisilane radical anion). Although an electronic structure similar to the acetylene radical anion has been suggested for the diethynylsilane anion radicals, the details are not yet clearly understood. Following the above arguments, the structure of acetylene radical anion can be very sensitive to substitution. Here we report an EPR study on the electronic structure of methylacetylene radical anion (MA^-), the simplest alkyl-substituted acetylene radical anion. The EPR spectrum was characterized by a large and anisotropic hf splitting due to the ethynyl proton as well as an anisotropic g-tensor. The anisotropic parameters were theoretically evaluated by *ab initio* and semiempirical MO methods. Comparing the experimental results with the theoretical ones, the electronic structure of MA^- is discussed.

Experimental

Chemicals used were: 2-methyltetrahydrofuran (2-MTHF), $CH_3C{\equiv}CH$ (MA) (Takachiho Kougyou, 99%), and $CD_3C{\equiv}CH$ (MA-d_3) (Takachiho Kougyou, 99 D atom%). 2-MTHF was used after drying with Na-metal. MA and MA-d_3 were used as received. Solid solutions of 1 mol% MA or MA-d_3 in 2-MTHF were prepared in a Spectrosil EPR sample tube on a vacuum line after several freeze and thaw cycles. The radical anion of MA was generated in a 2-MTHF glassy matrix by ionizing radiation using γ-rays from ^{60}Co at 77 K. Photo-illumination was provided by a tungsten-lamp with cut-off filters. EPR spectra were recorded on a Bruker ESP-300E spectrometer.

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The optimized structure was calculated by employing an *ab initio* method (GAUSSIAN 90/uhf/6-31+G**). For the excited states and corresponding energy calculations *ab initio*-CI methods were employed. Both isotropic and anisotropic (dipole) hyperfine (hf) coupling constants were evaluated based on the INDO spin densities for the optimized structure: the latter (dipole) terms were calculated using the program 'ANALDIP (analytical dipole)'.[10]

Results and discussions

(a) EPR spectra of methylacetylene radical anion. Fig. 1(a) shows the EPR spectrum of γ-irradiated 2-MTHF containing 1 mol% methylacetylene at 77 K. The spectrum consists of at least two components i.e., a sharp central singlet ($g=2.0023$) due to trapped electrons (e_t^-) and a broad quintet hf splitting of 1.9 mT attributable to 2-MTHF radical. By illuminating with light of $\lambda \geqslant 600$ nm, the singlet due to e_t^- disappeared with concomitant formation of a partially resolved doublet (marked as asterisks) as seen in Fig. 1(b). The newly appeared radical was observed only for the sample containing MA and was attributed to a solute radical. The results suggest that the partially resolved doublet is attributable to the MA radical anion (MA^-) formed by electron attachment to MA. By further illuminating with light of $\lambda \geqslant 350$ nm the spectrum due to MA^- disappeared completely and only the 2-MTHF radical was observed [Fig. 1(c)]. Parallel experiments were carried out by the electronic absorption spectroscopic method. Optical experiments conclusively support the EPR results. Here we only note that MA^- has an absorption maximum at $\lambda=360$ nm with resolved vibration bands of 1150 cm^{-1}. The EPR spectrum of MA^- was observed separately from the 2-MTHF matrix radical by subtracting the spectrum in Fig. 1(c) (2-MTHF radical) from that in Fig. 1(b). The MA^- spectrum obtained shows a complicated anisotropic doublet spread over 11.2 mT with a resolved quintet of 0.5 mT at the lower field. In order to determine precisely $\tilde{g}$ and $\tilde{A}$ principal values the experiments were repeated using MA-d_3. As the magnetic moment of D is smaller by a factor of ca. 6.5 than that of H, the deuterium substitution reduces the methyl proton hf splitting by the same amount so as to give it a linewidth of $\leqslant 0.4$ mT. Thus, the anisotropic doublet attributable to the ethynyl proton was clearly observed, which enabled us to determine the accurate principal values of the hf and *g*-tensors. The spectrum of MA^- in Fig. 1(d) was successfully simulated by using the following parameters: $A_{xx}=5.36$ mT, $A_{yy}=4.39$ mT, $A_{zz}=3.85$ mT for the ethynyl proton, $a=0.5$ mT for the methyl protons, and $g_{xx}=2.0005$, $g_{yy}=2.0020$, $g_{zz}=2.0021$ (Fig. 2).

Here we can unambiguously attribute the observed spectrum to the methyl acetylene radical anion for the following reasons. (1) A stable radical species was generated by reaction of MA with e_t^-. (2) The hf splittings due to the four protons of MA were clearly observed: one ethynyl proton and three equivalent methyl protons. (3) The large ethynyl proton hf splitting is close to that of acetylene radical anion (A^-): 4.53 mT (MA^-) vs. 4.8 mT (A^-).[6] (4) A vinyl-type radical formed by a hydrogen addition to MA is completely ruled out based on the experimental hf splittings.[11] The large and aniso-

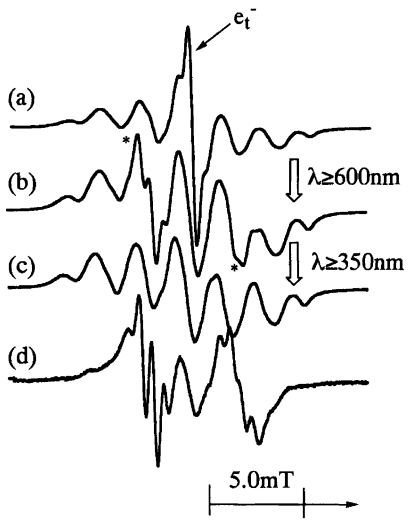

Fig. 1. EPR spectra of a solid solution of 2-MTHF containing 1 mol% of methylacetylene (MA) irradiated by γ-rays at 77 K: (a) observed immediately after γ-irradiation; (b) after illumination by light of $\lambda \geqslant 600$ nm; (c) after illumination by light of $\lambda \geqslant 350$ nm; (d) difference spectrum between (b) and (c). Spectra (c) and (d) are attributable to neutral 2-MTHF radical and the radical anion of MA (MA^-), respectively.

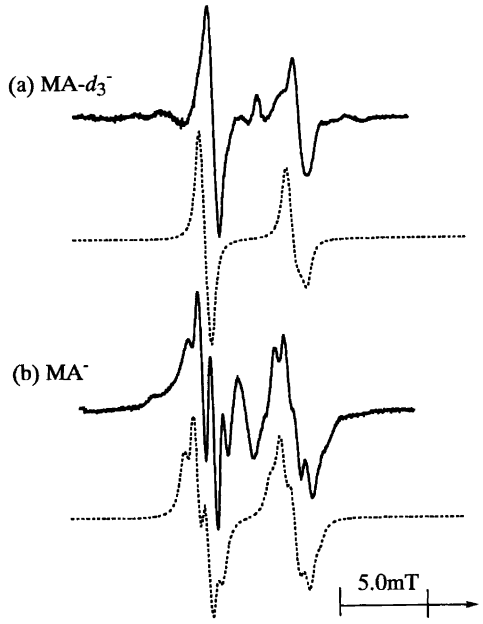

Fig. 2. Experimental EPR spectra of (a) MA-d_3^- and (b) MA^- in 2-MTHF matrix together with the simulated spectra (dotted lines) calculated using the ^1H hf splittings and *g*-values listed in Table 1.

tropic ethynyl proton hf splitting can be explained in terms of hyperconjugation with the unpaired electron orbital in a C_s structure as suggested by Muto for the acetylene radical anion.[6] It is noteworthy that the *in-plane* bent-structure results in less effective hyperconjugation to the methyl protons. In fact, the experimental ^{1}H hf splitting (0.5 mT) is smaller by five times than that of methyl proton in ethyl radical (2.7 mT).[12]

(b) ^{1}H hf splitting of MA$^-$. Structure optimization was carried out for both *trans-* and *cis-*forms of MA$^-$ in which the ethynyl proton and methyl protons occupied the positions out of the line of the C≡C triple bond. The calculated results are summarized in Fig. 3(a). The associated singly occupied molecular orbitals (SOMO) are also illustrated in the figure. Both *trans-* and *cis-*forms resulted in the *in-plane* C_s structure. For the *trans-*structure, the ethynyl and methyl groups have bent angles of 59.2° and 46.2°, respectively, with respect to the C≡C bond. For both structures one of methyl protons is located at the *cis-*position with respect to the triple bond and the SOMO has A' symmetry which consists of the *in-plane* p_y and p_z atomic orbitals.

Spin density distributions were calculated by the INDO MO method for both *trans-* and *cis-*optimized structures. ^{1}H hf principal values (b_{ij}) were then evaluated using eqn. (1), where N and K stand for nuclear spin and

$$b_{ij} = -\frac{1}{2} g\beta g_N \beta_N \langle S_z \rangle^{-1} \sum_{\mu\nu} \rho\mu\nu \langle \phi_\mu | r_{kN}^{-5} (r^2 kN \delta_{ij} - 3 r_{kN_i} r_{kN_j}) | \phi_\nu \rangle \quad (1)$$

electron spin, $\rho_{\mu\nu}$ a spin density matrix element related to atomic orbitals, ϕ_μ, and ϕ_ν and $i, j = x, y, z$. The calculations were carried out using the ANALDIP program[10] in which the INDO spin densities were employed.

The calculated hf principal values and axes of the ethynyl proton are summarized for the *trans-* and *cis-*structures in Fig. 3(c) and 3(d), respectively. The values are compared with the experimental ones in Table 1. The isotropic hf splittings of the ethynyl proton evaluated based on the INDO MO are 6.53 mT and 12.0 mT for the *trans-* and *cis-*structures, respectively; the former being closer to the experimental value, 4.53 mT. The ANALDIP calculations indicated in full anisotropy for the *trans-*structure, but axial symmetry for the *cis-*structure. The calculated anisotropic values for the *trans-*structure correspond rather well to the experimental ones with larger, middle, and smaller values on the x, y and z axes, respectively: the ^{1}H hf principal axes (x,y,z) coincide with the molecular axes (a,b,c) to within 1°.

In conclusion the ethynyl proton hf values of MA$^-$ can be explained rather well by the *trans-*structure, but not by the *cis-*structure, based on INDO and ANALDIP calculations, although the isotropic methyl proton hf splitting calculated for the *trans-*structure (1.37 mT), is larger by a factor of 2.7 than the experimental value of 0.5 mT.

(c) g principal values of MA$^-$. The experimental g-values of MA$^-$ are close to axial symmetry: $g_{xx} = 2.0005$, $g_{yy} = 2.0020$, $g_{zz} = 2.0021$. The g_{xx} value is negatively shifted from the free electron value (2.0023), but the other two components remained unshifted. The theoretical g-values were calculated for the *trans-* and *cis-*optimized structures of MA$^-$ and compared with the experimental ones. Eqn. (2) was used to calculate the principal values of g_{ii} ($i = x, y, z$), where ϕ_0 and ϕ_n are the ground and

$$g_{ii} = 2.0023 - 2 \sum_n \sum_{k,j} \frac{\langle \phi_0 | \zeta_k L_{ik} \delta_k | \phi_n \rangle \langle \phi_n | L_{ij} \delta_j | \phi_0 \rangle}{E_n - E_0} \quad (2)$$

excited state molecular orbitals, E_0 and E_n the corresponding energies. L_{ik} and L_{ij} are the i-component of

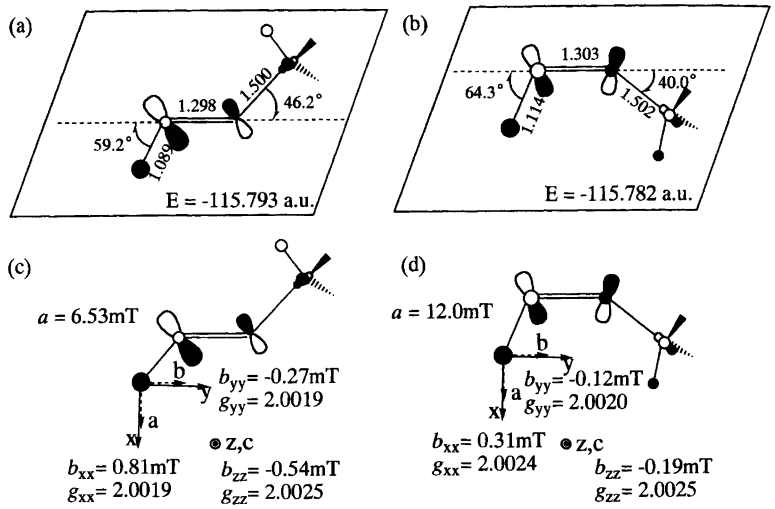

Fig. 3. Optimized structures and SOMO of (a) *trans-* and (b) *cis-*methylacetylene radical anions by the *ab initio* method (GAUSSIAN 90/uhf/6-31+G**). Theoretical principal values and axes of the ^{1}H hf tensor and g-tensor for (c) *trans-* and (d) *cis-*methylacetylene radical anions are also shown. The calculations were carried out for the optimized structures obtained by the *ab initio* MO method. See the text for details.

Table 1. Experimental ^{1}H hf splittings and *g*-values of methylacetylene radical anion together with calculated values.

	^{1}H hf (/mT)							
	1H				3H	*g*-values		
	a	b_{xx}	b_{yy}	b_{zz}	*a*	g_{xx}	g_{yy}	g_{zz}
$CH_3C{\equiv}CH^-$ (exp.)	4.53	0.83	−0.14	−0.68	0.5	2.0005	2.0020	2.0021
trans-$CH_3C{\equiv}CH^-$ (calc.)	6.53	0.81	−0.27	−0.54	1.37	2.0019	2.0019	2.0025
cis-$CH_3C{\equiv}CH^-$ (calc.)	12.0	0.31	−0.12	−0.19	0.97	2.0024	2.0020	2.0025

orbital angular momentum operator, and ξ_k is the spin-orbital coupling constant for the *k*th atom. The orbitals (ϕ_0 and ϕ_n) and energies (E_0 and E_n) were evaluated by a semiempirical AM1 method for the optimized structures. Furthermore the principal axes were assumed to be the same as those of the hf tensor. The calculated *g*-values are compared with the experimental ones in Table 1 together with the hf values. In the above section the SOMO of MA^- was concluded to be of *a'* symmetry which consisted of the *in-plane* p_y and p_z atomic orbitals. The negative shift in g_x might originate from the contribution of the orbitals located above the SOMO and which have the same symmetry. Similarly to the hf splittings, the *g*-values agree better with the *trans*-structure than with the *cis*-structure. A negative shift in g_x is qualitatively reproduced in the calculations, but with smaller values. The smaller negative shift may arise from the fact that the AM1 calculations overestimate the energies differences, $E_n - E_0$. Note that for the *cis*-structure, positive and negative shifts were calculated for g_x and g_y, respectively. The results are inconsistent with the experimental data. Thus, the *trans*-bent structure of MA^- was also supported by the *g*-value calculations.

Concluding remarks

The anion radical of methylacetylene (MA^-) was generated in a glassy 2-MTHF matrix by ionizing irradiation at 77 K and subjected to an EPR study. The EPR parameters ($\tilde{A}$ and $\tilde{g}$) were determined with the help of methyl-deuteriated methylacetylene (MA-d_3). The anisotropic ^{1}H hf and *g*-values were theoretically calculated by *ab initio* and semiempirical MO methods. From a comparison of the experimental values with the theoretical ones, a *trans*-bent structure with an *a'* SOMO was deduced for MA^-.

Parallel experiments were performed using electronic absorption spectroscopy. It appeared that MA^- has an absorption maximum at 360 nm with vibration bands of 1150 cm^{-1}. The bands are attributable to an electronic transition to an excited state with *A'* symmetry and *trans*-deformation vibrations, respectively. The details of the optical spectrum will be published elsewhere.[13]

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