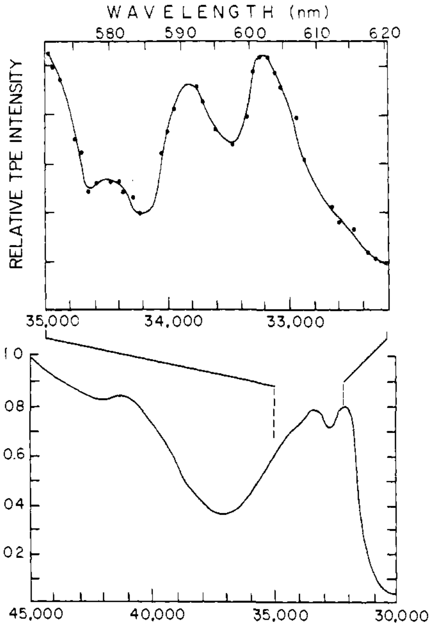

Figure 1. Lower trace: absorption spectrum of Rh(CN)$_2$(dmb)$_2^+$, ~10^{-6} M in 4:1 ethanol–methanol at room temperature. The hatch marks indicate the energy range of correspondence between the absorption spectrum and the two-photon spectrum. Upper trace: two-photon excitation spectrum of Rh(CN)$_2$(dmb)$_2^+$ at 77 K. The upper x-axis scale represents the laser wavelengths (nm) used to generate the spectrum, and the lower x-axis scale corresponds to the actual energies (cm^{-1}) of excitation. Rh(CN)$_2$(dmb)$_2^+$ emission monitored at 471 nm.

with an increased peak-to-average power ratio.

The TPE spectrum and the absorption spectrum of Rh(CN)$_2$(dmb)$_2^+$ are shown in the upper and lower half of Figure 1, respectively. The corresponding profiles of the two spectra are entirely different, indicating that unique bands are accessed. We believe that the origin of the structure seen in the TPE spectrum is attributable to metal-localized d → d* transitions rather than to ligand-localized transitions. The absorption spectra of tris(4,4′-dimethyl-2,2′-bipyridine)rhodium(III) and Rh(CN)$_2$(dmb)$_2^+$ are almost identical, since the major bands in both spectra are intraligand $\pi \rightarrow \pi^*$ transitions that are not greatly perturbed by the change in the crystal field splitting between the two ions. However, TPE of Rh(dmb)$_3^{3+}$ was not observed, although the two complexes have similar luminescence intensities when viewed under single-photon excitation. Thus, it appears in Rh(CN)$_2$(dmb)$_2^+$ that the increased crystal field splitting due to the substitution of the cyano groups for a bipyridine has moved a d → d* band(s) into the energy region we are accessing. Estimation of the positions of d → d* transitions via crystal field considerations supports the above conclusion.

Rh(CN)$_2$(dmb)$_2^+$ is a pseudooctahedral d^6 complex with the low-spin configuration t$_2^6$. The excited state configuration t$_2^5$e gives rise to a pair of singlet d → d*'s and a pair of triplet d → d*'s that are split due to the C_{2v} symmetry of the complex. The states are not strictly gerade, thus the two-photon excited d → d* transitions are less allowed than similar TPE transitions would be for an octahedrally symmetric molecule. We have estimated experimentally that the TPE efficiency for the transitions falls at least an order of magnitude below a "forbidden" two-photon transition (the vibronically coupled $A_{1g} \rightarrow B_{2u}$ transition in naphthalene). This suggests that they are due to the triplet d → d* states, where the spin-forbidden nature of the triplet state transition and loss of gerade character have greatly decreased the TPE intensity. Extension of the Rh(CN)$_2$(dmb)$_2^+$ spectrum and excited-state symmetry studies of the spectral features via two-photon techniques are necessary before absolute assignments can be made.

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Static Distortion of ^{2}E Molecular Cations of Cyclobutane at 4.2 K Giving ^{2}B$_2$ with C_{2v} Symmetry and Its Dynamic Average at $\gtrsim$77 K: ESR Evidence

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Highly symmetric molecular radical cations of simple alkanes often provide important examples of Jahn–Teller (J–T) active species, and the elucidation of the J–T distorted structure must be of fundamental significance in chemistry. However, little is known about the static distortion of these J–T active σ radical cations. Recent development of radiolytic production of radical cations in CFCl$_3$[1] and in other halogenated matrices[2,3] has made it possible to study electronic and geometrical structures of such J–T active species by electron spin resonance spectroscopy.[2,4-7] These results suggest that direct experimental information on static distoriton of J–T active species can be gathered at quite low temperatures even for small molecules with near orbital degeneracy.[2,7] In the present work, joint research by the two groups has been undertaken to elucidate a distorted structure of c-C$_4$H$_8^+$, one of the most important J–T active species.

The molecular cations were radiolytically produced at 77 or 4.2 K in a frozen solution of CFCl$_3$ containing a dilute solute of c-C$_4$H$_8$ (1:423 by volume).[1] Figure 1, parts a–d, demonstrates the ESR spectra measured at temperatures attainable by the instrument in Kyoto for the samples γ-irradiated at 77 K. At temperature above 77 K the fairly isotropic nine-line spectral feature indicates that the possible Jahn–Teller distortion is averaged out at these temperatures to result in an average splitting constant of about 15–16 G. Upon lowering the temperature the outer peaks are broadened as shown in Figure 1, parts a–d.

Shown in Figure 2 are the spectra obtained from the sample X irradiated at 4.2 K in Nagoya. The 4 K spectrum observed immediately after irradiation (Figure 2a) consists of three lines with the separation of 49 G, which further splits into three lines with the separation of 14 G. After annealing the sample at 77 K for 2 min, the coupling constants of the 3 × 3 line spectrum irreversibly changed into 44 and 22 G with a considerable narrowing of the line width giving a substructure of about 5 G (Figure

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(1) (a) Shida, T.; Kato, T. *Chem. Phys. Lett.* **1979**, *68*, 106. (b) Shida, T.; Egawa, Y.; Kubodera, H.; Kato, T. *J. Chem. Phys.* **1980**, *73*, 5963.

(2) (a) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Am. Chem. Soc.* **1981**, *103*, 3591. (b) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Chem. Phys.* **1982**, *77*, 5891.

(3) (a) Symons, M. C. R.; Smith, I. G. *J. Chem. Res., Synop.* **1979**, 382. (b) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Phys. Chem.* **1981**, *85*, 2149.

(4) Takemura, Y.; Shida, T. *J. Chem. Phys.* **1980**, *73*, 4133.

(5) (a) Kubodera, H.; Shida, T. 23rd Symposium of Radiation Chemistry, B202, October 1980, Kyoto. (b) Kubodera, H.; Shida, T. 19th ESR Symposium, 22A05, October 1980, Yokohama. (c) Shida, T.; Takemura, Y. *Radiat. Phys. Chem.* **1983**, *21*, 157.

(6) Ohta, K.; Nakatsuji, H.; Kubodera, H.; Shida, T. *Chem. Phys.* **1983**, *76*, 271.

(7) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 202.

0002-7863/83/1505-5496$01.50/0

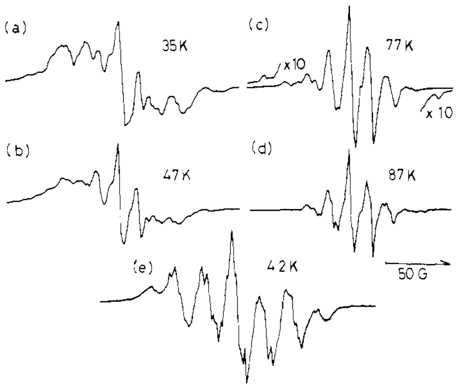

Figure 1. The ESR spectra observed for γ-irradiated cyclobutane in $CFCl_3$ (1:423 by volume). The sample was irradiated at 77 K and the spectra were measured at the temperatures indicated in the figure. Spectra a–d were measured in Kyoto whereas spectrum e was measured in Nagoya.

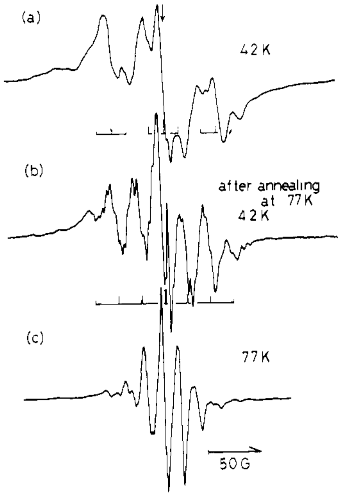

Figure 2. The ESR spectra observed for X-irradiated cyclobutane in $CFCl_3$ (1:423 by volume). The sample was irradiated at 4.2 K and the spectra were measured at 4.2 K (a) immediately after the irradiation; (b) after annealing at 77 K for two min; (c) measured at 77 K.

2b). Although the observing temperature was lowered further down to 1.6 K, the spectral feature did not change at all. As shown in Figure 1e, the sample γ-irradiated at 77 K also gives essentially the same spectrum at 4.2 K as that observed after the annealing at 77 K following the irradiation at 4.2 K. As shown in Figure 2c, the spectral feature of the 4 K sample reversibly changes at 77 K into the one that is the same as that of the sample irradiated at 77 K (Figure 1e).

These results clearly indicate that c-$C_4H_8^+$ exhibits static distortion at 4.2 K like c-$C_3H_6^+$, and the dynamic average takes place at elevated temperatures.[7] The 4 K spectrum shows that four out of eight protons give a pair of large hyperfine couplings of 49 (44) and 14 (22) G, and the rest give small hyperfine couplings of about 5 G. On the assumption of the positive sign for the coupling constants of 49 (44) and 14 (22) G and the negative sign for the small coupling of 5 G, which is resolved after the annealing, the averaged proton coupling constant is obtained to be 13.3 (14.0) G in agreement with the observed value of 15–16 G at 77 K.. The reasons for the negative sign are given below.

Now, c-C_4H_8 is known to have a puckered ring structure with D_{2d} symmetry,[8] and the highest occupied level is a doubly degenerate e orbital. After a loss of an electron forming molecular cations, the orbital degeneracy may be removed by the molecular distortion due to the Jahn–Teller instability. Since the Jahn–Teller active vibrational modes are the b_1 and b_2 ring deformation,[6,9,10] the expected symmetry reductions are to D_2 and C_{2v}, respectively, as shown in Figure 3a. Since the D_2 structure requires at least four equivalent protons, the observed 3 × 3 line spectrum cannot be attributable to the D_2 distortion. On the other hand, the C_{2v} structure can give a pair of two equivalent protons.

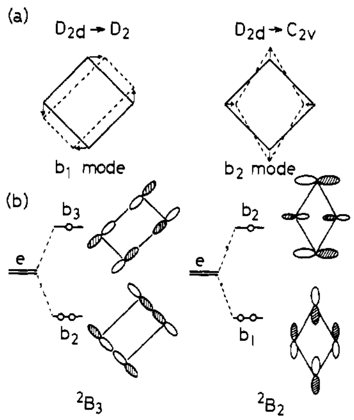

Figure 3. (a) The two kinds of Jahn–Teller active vibrational modes of c-$C_4H_8^+$ with D_{2d} symmetry; (b) The splitting of orbital degeneracy and the schematic orbitals expected for the b_1 and b_2 distortions.

The degenerate e orbital splits into b_1 and b_2 in the C_{2v} deformation whereas into b_2 and b_3 in the D_2 deformation as shown in Figure 3b. Both the b_1 and b_2 orbitals with C_{2v} symmetry can give the two large and the two small equivalent proton couplings in agreement with the observation at 4.2 K. However, since the deformations giving the b_1 and b_2 orbitals strengthen the bonding and antibonding nature of the cross-overlapping of the C_2 and C_4 orbitals, respectively, the b_2 orbital is expected to become an unpaired electron orbital.

The trial INDO MO calculations for the distorted structures gave the coupling constants qualitatively consistent with the observations, that is, +50.5 and +25.5 G for the equatorial and axial protons respectively attached to the C_2 and C_4 atoms, whereas −7.9 and −11.9 G are obtained for the equatorial and axial protons respectively attached to the C_1 and C_3 atoms.[11] The negative coupling to the C_1 and C_3 protons is consistent with the assumption of the negative sign for the coupling of 5 G.

The irreversible change of the equatorial and polar proton couplings after annealing at 77 K can be explained by the slight flattening of the puckered ring. Alternatively, it may be accounted for in terms of the partial average due to the zero-point ring-puckering motion, if the potential barrier is lowered by the thermal annealing.

As for the dynamic average, simple rapid ring-puckering motion makes the equatorial and axial proton couplings equivalent. However, the C_1 and C_2 proton couplings do not become equivalent without taking the dynamic average associated with the Jahn–Teller active b_2 vibration into consideration. Although the alternative explanation in terms of matrix effects cannot be excluded, that is, the matrix effect that reduces the molecular symmetry into C_{2v} at 4.2 K, and the rapid rotation around the C_2 axis at 77 K, which averages the C_{2v} matrix effect, the static and dynamic J–T effect seems to be more attractive.

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Registry No. Cyclobutane, 287-23-0; cyclobutane radical cation, 34474-99-2.

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[8] (a) Dunitz, J. D.; Schomaker, V. *J. Chem. Phys.* **1952**, *20*, 1703. (b) Almenningen, A.; Bastiansen, O.; Skancke, P. N. *Acta Chem. Scand.* **1961**, *15*, 711.

[9] Herzberg, G. "Molecular Spectra and Molecular Structure III Electronic Spectra and Molecular Structure of Polyatomic Molecules"; Van Nostrand: New York, 1966; p 50.

[10] Liehr, A. D. *J. Phys. Chem.* **1963**, *67*, 389.

[11] The geometry assumed is as follow: $r_{CC} = 1.593$ Å, $\angle C_1C_2C_3 = 109.3°$, $\angle C_2C_3C_4 = 68.9°$, $r_{CH} = 1.098$ Å, $\angle HCH = 114°$.