NSF and the Dreyfus Foundation contributed to purchase of the NMR spectrometer.

Registry No. $H_2PO_2^-$, 15460-68-1; Zn, 7440-66-6; Cd, 7440-43-9; Mg, 7439-95-4; Li, 7439-93-2; Ca, 7440-70-2; Sr, 7440-24-6; Na, 7440-23-5; Ba, 7440-39-3.

Supplementary Material Available: Original data on $^1J_{PH}$ and $^1J_{PD}$ (4 pages). Ordering information can be found on any current masthead page.

Valence Isomerization of the Radical Cations of Bicyclopentanes in γ-Irradiated Low-Temperature Freon Matrices

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Abstract: The radical cation of spiro[2.2]pentane was produced in a γ-irradiated CCl_3F matrix at 4 K. Analysis of the observed ESR spectrum has led, by a process of elimination, to the conclusion that the radical cation is probably Jahn–Teller (J–T) distorted from D_{2d} to C_{2v}. At 77 K the distorted radical cation isomerizes to the radical cation of methylene cyclobutane. Above 77 K the latter shows a reversible ESR spectral change which may be interpreted in terms of the isomerization to a nonclassical radical cation. The radical cation of bicyclo[2.1.0]pentane isomerizes even at 4 K to the radical cation of cyclopentane. The results are discussed in comparison with ab initio MO calculations.

In view of the recent studies of the ring opening of the radical cations of cyclopropane and its derivatives under particular experimental conditions,[1] it seemed interesting to extend the study to bicyclic hydrocarbons bearing the cyclopropyl ring. Two examples of such systems, spiro[2.2]pentane and bicyclo[2.1.0]pentane, were studied in the present work by the Freon matrix technique originally proposed by one of the present authors.[2,3] The homolysis of the neutral radicals derived by hydrogen abstraction from these pentanes has been reported previously.[4]

We have obtained an ESR spectrum for the radical cation of spiropentane in the Freon matrix at 4 K which is not incompatible with the assumption that the radical cation is J–T distorted from D_{2d} to C_{2v}. The distorted radical cation suffers a ring opening at 77 K to isomerize to the radical cation of methylenecyclobutane. The ESR spectrum of the latter changes reversibly between 77 K and ~150 K which may indicate the occurrence of a nonclassical radical cation.

As for the radical cation of bicyclo[2.1.0]pentane, it isomerizes to the radical cation of cyclopentane even at 4 K. The observed results have been substantiated by ab initio UHF MO calculations with the STO-3G and 4-31G basis sets.

Experimental and Computational

The two bicyclopentanes were prepared by the method in the literature.[4] Each of the hydrocarbons was dissolved in CCl_3F with concentrations of 0.2–0.5 mol % and γ-irradiated in a Suprasil ESR cell at 4 K, 77 K, and various temperatures up to ~150 K. The general description of the Freon matrix technique to obtain the solute radical cations has been described elsewhere.[2,3,5]

The optimum geometries of the various isomers were calculated by the GRADIENT method incorporated in the Gaussian 80 program with the approximation of UHF and the STO-3G and 4-31G basis sets.

Results and Discussion

(1) The Radical Cation of Spiro[2.2]pentane at 4 K. As in the case of allene the radical cation of spiropentane should be distorted from D_{2d} to either D_2 or C_{2v} by the J–T effect.[6] In both cases the total eight protons will be divided into two groups of four positionally equivalent protons (see the bottom of Figure 1). According to the following reasoning (i–iii), the possibility of the D_2 deformation is eliminated and that of C_{2v} is favored.

(i) Geometry Optimization with the Symmetry Restrictions of D_2 and C_{2v}. The result obtained with the 4-31G basis set is illustrated in Figure 1. The total energies were −193.3152 and −193.3249 hartrees for D_2 and C_{2v}, respectively. In the D_2 conformation the two cyclopropyl rings assume acute isosceles triangles, with an angle of 54.6° between the planes of the rings. In the C_{2v} conformation both rings have obtuse isosceles structures, but the two upper methylene groups of Figure 1 are almost in an sp^2-hybridized state. The deformations are understandable as follows. In the D_2 conformation the highest singly occupied MO (see the bottom of Figure 1) is related to the antisymmetric component of the degenerate HOMO (3e′) of cyclopropane.[7-9] Since this component is characterized as bonding between the central and the methylene carbon atoms, the depletion of one electron from the HOMO of the parent molecule should stretch the bonds as found. Likewise, we can consider that in the C_{2v} conformation one electron has been lost from the symmetric component of the degenerate HOMO of one of the two orthogonal cyclopropane rings, which should weaken the C–C bond between the two adjacent methylene groups. Unlike the D_2 conformation the odd electron is found localized mostly in one of the cyclopropyl units, causing the remarkable bond stretching in one of the two

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(1) (a) Qin, X.-Z.; Williams, Ff. *Chem. Phys. Lett.* **1984**, *112*, 79. (b) Qin, X.-Z.; Snow, L. D.; Williams, Ff. *J. Am. Chem. Soc.* **1984**, *106*, 7640. (c) Symons, M. C. R. *Chem. Phys. Lett.* **1985**, *117*, 381. (d) Qin, X.-Z.; Snow, L. D.; Williams, Ff. *Chem. Phys. Lett.* **1985**, *117*, 383.

(2) Shida, T.; Kato, T. *Chem. Phys. Lett.* **1979**, *68*, 106.

(3) Shida, T.; Egawa, Y.; Kubodera, H.; Kato, T. *J. Chem. Phys.* **1980**, *73*, 5963.

(4) (a) Bews, J. R.; Glidewell, C.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1447. (b) Jamieson, C.; Walton, J. C.; Ingold, K. U. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1366. (c) Kennedy, A. J.; Walton, J. C.; Ingold, K. U. *J. Chem. Soc., Perkin Trans. 2* **1982**, 751. (d) Stirling, C. J. M. *Tetrahedron* **1985**, *41*, 1613.

(5) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180.

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

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

(8) Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1983**, *61*, 2310.

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

0002-7863/86/1508-2805$01.50/0

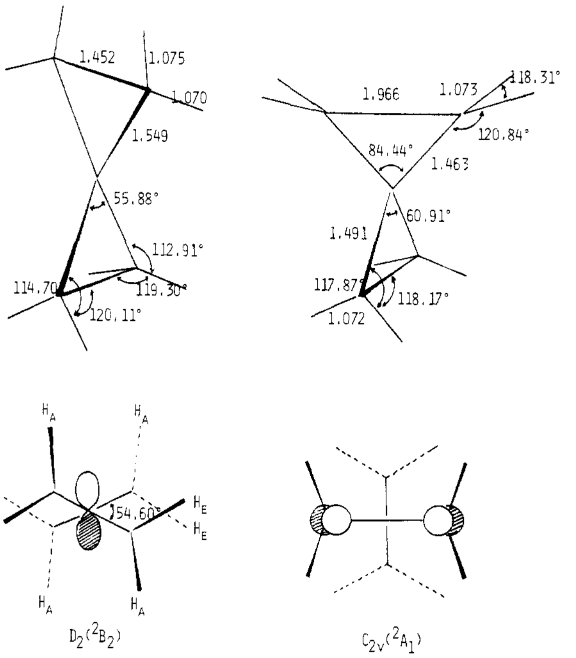

Figure 1. Optimized geometries of the D_2- and C_{2v}-deformed radical cations of spiropentane. The calculation was made with the UHF-4-31G approximation by the GRADIENT method. The lobes represent schematically the patterns of the highest singly occupied molecular orbitals.

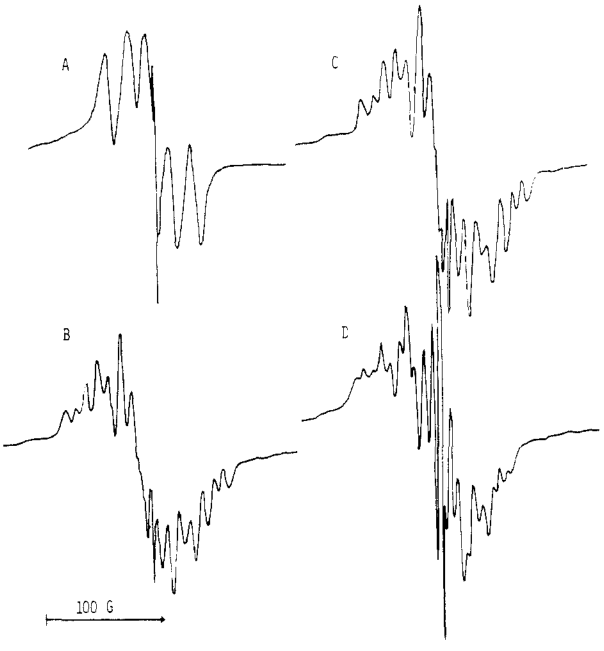

Figure 2. (A) ESR spectrum of spiropentane irradiated and measured at 4 K. (B) Same as above but measured at 77 K. (C) ESR spectrum of methylenecyclobutane irradiated and measured at 77 K. (D) Same as above but measured at higher temperatures of ~150 K. The spectrum changes reversibly to Figure 2C upon recooling at 77 K.

cyclopropane rings as mentioned above.

In the geometry optimization of the C_{2v} conformation the result in Figure 1 was attained even if the upper methylene groups were deliberately rotated by up to ~30° around the axis connecting the central and the methylene carbon atoms, both in conrotatory and disrotatory ways. Therefore, the C_{2v} conformation in Figure 1 should, indeed, correspond to a local minimum attainable from the nascent D_{2d} radical cation. It should be noted that the elongated bond with the length of 1.966 Å would allow the two upper methylene groups with an sp^2 character to rotate around the axis connecting the central and the methylene carbon atoms provided that the matrix does not cause a significant hindrance.

(ii) INDO Calculation for the Proton hfc Constants of Both the D_2 and C_{2v} Conformations and ESR Measurement of the Radical Cation at 4 K. The result of the calculation is $a(4H_a) = 28.8$ G and $a(4H_e) = 1.4$ G for D_2 where H_a and H_e stand for the axial and equatorial protons as shown in Figure 1 and $a(4H_{upper}) = -11.4$ G and $a(4H_{lower}) = -3.7$ G for C_{2v}.

The observed spectrum of spiropentane in CCl_3F irradiated and measured at 4 K is shown in Figure 2A which should be regarded as a superposition of the signals due to the radical cation of spiropentane, the matrix radical, and the color center in the sample cell. However, as shown previously,[2,3] the contribution from the latter two is considered negligible, so that the main feature of the spectrum of the radical cation of our interest is a quintet with $a = 18$ G. Although neither of the calculated hfc constants fits decisively the observed 18 G, the fact that the calculated constant of one group of four equivalent protons is small enough to be absorbed in the observed line width (<10 G) of the quintet indicates that the D_{2d} cation is, indeed, J–T distorted whether the deformation is a D_2 or a C_{2v} mode. However, the intensity distribution of the quintet is not binominal which will be discussed below.

(iii) Discussion of the Intensity Distribution of the Spectrum in Figure 2A. The non-binominal intensity distribution of the ESR hyperfine structure of radicals with a relatively large rotational constant such as $NH_2^{\cdot}$ and $CH_3^{\cdot}$ in matrices at low temperatures has been explained by invoking the nuclear spin statistics under the assumption of the free rotation.[10] If the same argument is applied naively to the present radical cation, whether it is in the D_2 or the C_{2v} conformation, we should note that the total wave function ($\simeq\psi_{ele}\psi_{vib}\psi_{rot}\psi_{NS}$) must be symmetric for the two exchanges of four identical fermions in pairs by a 180° rotation about one of the C_2 axes. This restricts the nuclear spin function, ψ_{NS}, by the known process[10] to lead to a non-binominal intensity distribution.

However, the principal values of the rotational constants of the D_2 and C_{2v} radical cations in Figure 1 are 0.12, 0.14, 0.38 and 0.14, 0.15, 0.29 cm^{-1}, respectively, which are one order of magnitude smaller than kT at 4.2 K. Thus, if the radical cation rotates freely in the matrix, it is incompatible to assume the predominance of the rotational level of $J = 0$ which is a prerequisite to the argument developed by McConnell.[10] The population in the states of $J > 0$ should obliterate the regulation by the nuclear spin statistics and the intensity distribution should be approximated by the binominal distribution.

If, on the other hand, the radical cation is confined in cages with sizable barriers to rotation, the Pauli principle is not demanded and the hyperfine pattern should be characterized by a normal binominal intensity distribution. Therefore, there seems to be a dilemma in reconciling the predicted quintet with the normal binominal intensity distribution with the observed spectrum in Figure 2A. There seems, however, to be a chance that the C_{2v} conformation can explain the observed result: Since the optimized geometry of the C_{2v} conformation in Figure 1 seems to allow rotation of the upper methylene groups, whether it is rather free or hindered only to such an extent as to keep near equivalence of the two pairs of the fermions, some quantum effect in the methylene protons similar to that operative in $NH_2^{\cdot}$ and $CH_3^{\cdot}$ in matrices might be conceived. At present we have no transparent mechanism which clarifies the relation between the observed result and the proposed "local" rotation of the methylene groups. However, the above argument rules out, at least, the alternative possibility of D_2 deformation, so we maintain that the C_{2v} possibility remains viable.

(2) The Radical Cation of Spiro[2.2]pentane at 77 K. When the solution of spiropentane in CCl_3F irradiated at 4 K was examined at 77 K, the spectrum in Figure 2A changed irreversibly to that in Figure 2B. The same spectrum was obtained when the sample was irradiated at 77 K and measured at the same temperature. Essentially the same spectrum was obtained when methylenecyclobutane in CCl_3F (0.2–0.5 mol %) was irradiated

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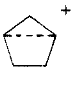
(10) McConnell, H. M. J. *Chem. Phys.* **1958**, *29*, 1422.

Table I. Total Energies of the Various $C_5H_8^+$ for Their Optimized Geometries Obtained by UHF-STO-3G Calculations (hartree)[a]

(1) spiro[2.2]pentane (D_2)	−191.3293
(2) spiro[2.2]pentane (C_{2v}, "face-to-face")	−191.3299
(3) spiro[2.2]pentane (C_{2v}, "edge-to-edge")	−191.3560
(4) methylene cyclobutane	−191.4019
(5) bicyclo[2.1.0]pentane	−191.3395
(6) bicyclo[2.1.0]pentane (1,3-bond, broken)	−191.3990
(7) cyclopentene	−191.4415

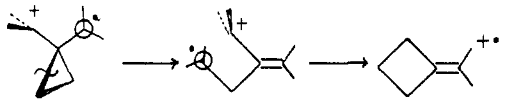
[a] The geometries of the first two entries were very close to those given Figure 1 which are obtained by a better basis set of 4-31G. The geometry of entry 5 is assumed to be the same as that of the neutral molecule computed by the RHF-STO-3G approximation. The geometry of entry 6 may be schematized as



and measured at 77 K as shown in Figure 2C. Although it is not straightforward to reproduce the spectrum in Figure 2C by simulation, as in the case of the radical cation of propylene,[11] spectra B and C of Figure 2 are assigned to the radical cation of methylenecyclobutane in view of the success of obtaining the radical cations of a number of simple olefins under the same experimental condition.[3]

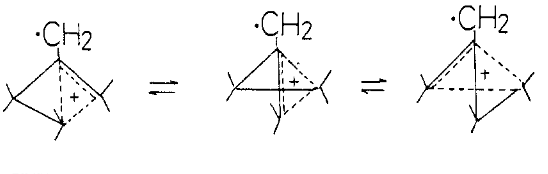
The first two entries of Table I correspond to the D_2 and C_{2v} radical cations of spiropentane in Figure 1, but the basis set to compute the optimized geometries and the total energies was simplified from 4-31G to STO-3G. The same simplified basis set was used for the rest of the entries in Table I to save computer time. It is noted that the radical cation of methylenecyclobutane is significantly exothermic relative to the first three entries in Table I, and we anticipate that the same trend of exothermicity will also be predicted with the 4-31G basis set. The significant exothermicity of entry 4 relative to entry 2, which is assumed to correspond to the C_{2v} radical cation in Figure 1, is consistent with the facile isomerization from entry 2 to entry 4 upon warming from 4 to 77 K. (Entry 3 is calculated just for test. In the overall isomerization from entry 2 to entry 4 the local minimum of entry 3 may be overlooked and the reaction in eq 1 may proceed easily.)

In the case of the radical cation of the prototype cyclopropane the ring is considered to open to yield a "face-to-edge" conformation.[1] By analogy with the ring opening of the cyclopropyl methyl radical to the but-3-enyl radical[4] the following reaction is easily conceivable.



(1)

(3) The Radical Cation of Methylenecyclobutane at 77–150 K. The reversible change between spectra C and D in Figure 2 observed whether we started from spiropentane or methylenecyclobutane attracted our interest: the spectrum in Figure 2D may be regarded as a triple-septet which indicates that the protons are grouped into two and six equivalent protons. Simulations suggest a set of 5 G (2 H) and 19 G (6 H). Although it is possible that the molecular motion of the radical cation of methylenecyclobutane at the higher temperatures causes accidentally two and six protons to have similar hfc constants, an alternative interpretation is that the radical cation is in the equilibrium in eq 2 and 3. A similar equilibrium for the nonclassical carbonium ion of $C_4H_7^+$ has been vigorously debated.[12-13] In eq 2 and 3, of course, the odd electron is not confined in the methylene group atop the tetrahedron. We propose tentatively that one of the methylene units is slightly different from the other three in the hydride shuffling. If this interpretation is correct, the ion should be regarded as a nonclassical radical cation which is without precedent as far as we know,



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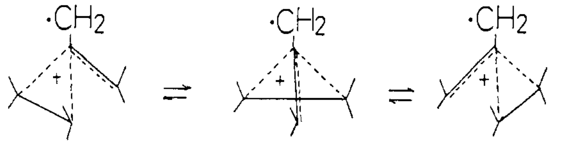
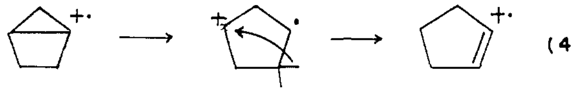


(3)

(4) The Radical Cation of Bicyclo[2.1.0]pentane. Bicyclo[2.1.0]pentane in CCl_3F irradiated at 4 and 77 K gave a spectrum identical with that of the radical cation of cyclopentene.[3] The result is consistent with the calculation summarized in the fifth to seventh rows of Table I, The calculation was made by using the same UHF-STO-3G basis set as for entries 1–4 to find the optimum geometries except for the one in the fifth row: the geometry of the fifth entry was determined first for the neutral molecule with the RHF-STO-3G approximation, and then the total energy was calculated by the UHF-STO-3G for the radical cation assumed to be in the same configuration as the calculated neutral molecule, However, this configuration is unstable for the radical cation and the geometry converged from the one in the fifth row to that in the sixth row. In the latter the 1,3-bond in the cyclopropyl ring has been broken, as in the case of the radical cation of cyclopropane.[1] The five-membered ring retains a C_s symmetry. The result for this geometry is given in the sixth row of Table I. Finally, the total energy of the optimized geometry of the cyclopentene radical cation is given in the seventh row. The differece of energies in the fifth and seventh rows is large enough for the overall isomerization to the radical cation of cyclopentene to be expected. The actual mechanism of isomerization may be that the nascent radical cation corresponding to the fifth row finds the local minimum of the sixth row, but this is followed by a 1,2- and/or 1,3-hydride transfer to complete the isomerization.



(4)

We have presented experimental and computational evidence for the isomerization of the radical cations of the two bicyclopentanes. A CIDNP study would be pertinent to see whether the radical cations proposed in the present work are involved in the photoinduced electron transfer in systems of the bicyclopentanes containing suitable electron acceptors as shown for various cases.[14]

Acknowledgment. Some of the computations were carried out at the Institute for Molecular Science, Okazaki, Japan. The study was partially supported by the Subsidy for Scientific Research of the Ministry of Education in Japan, Grant No. 59430004. The authors (K.U. and T.S.) are indebted to Professor Koichi Itoh for his remark on the rotation of radical cations in the solid. They thank Dr. Akira Kira for his generosity to allow them to use the ESR facility at the Institute of Physical and Chemical Research, Wako, Japan.

Registry No. Spiro[2.2]pentane, 157-40-4; bicyclo[2.1.0]pentane, 185-94-4; spiro[2.2]pentane radical cation, 101517-28-6; bicyclo[2.1.0]pentane radical cation, 101493-03-2; cyclopentene radical cation, 34512-37-3; methylenecyclobutane radical cation, 91631-64-0.

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(11) Toriyama, K.; Nunome, K.; Iwasaki, M. *Chem. Phys. Lett.* **1984**, *107*, 86.

(12) Olah, G. A.; Kelly, D. P.; Jeuell, C. L.; Porter, R. D. *J. Am. Chem. Soc.* **1970**, *92*, 2544.

(13) Staral, J. S.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J.; Olah G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8016.

(14) For example: Roth, H. D.; Schilling, M. L. M.; Wamser, C. C. *J. Am. Chem. Soc.* **184**, *106*, 5023.