Static Distortion of Radical Cations of Cyclopropane at 4.2 K: E.S.R. Evidence†

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E.s.r. evidence has been obtained that cyclopropane cations exhibit a static distortion from D_{3h} to C_{2v} symmetry in a matrix at 4.2 K; the 3e′ (D_{3h}) highest occupied degenerate orbital splits into $6a_1$ and $3b_1$ (C_{2v}) orbitals and the unpaired electron occupies $6a_1$, giving dominant spin densities on the two basal carbon atoms.

Recently we have found that $C_2H_6^+$, a Jahn–Teller active molecule, trapped in SF_6 shows a reversible temperature change which may be ascribable to static and dynamic Jahn–Teller effects.[1] Cyclopropane (cyclo-C_3H_6) with D_{3h} symmetry possesses a degenerate highest occupied orbital (3e′) so that cyclo-$C_3H_6^+$ is also a Jahn–Teller active molecule. Recently Shida and co-workers[2] have observed the e.s.r. spectrum of cyclo-$C_3H_6^+$ produced in $CFCl_3$ at 77 K and have explained the extremely small hyperfine couplings giving an

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† Preliminary results were presented at the 46th Autumn Annual Meeting of the Chemical Society of Japan, 3rd October, 1982, Niigata, Abstract p. 13; details were presented at the 21st E.s.r. Symposium, 26th October, 1982, Tsukuba, Abstract p. 48.

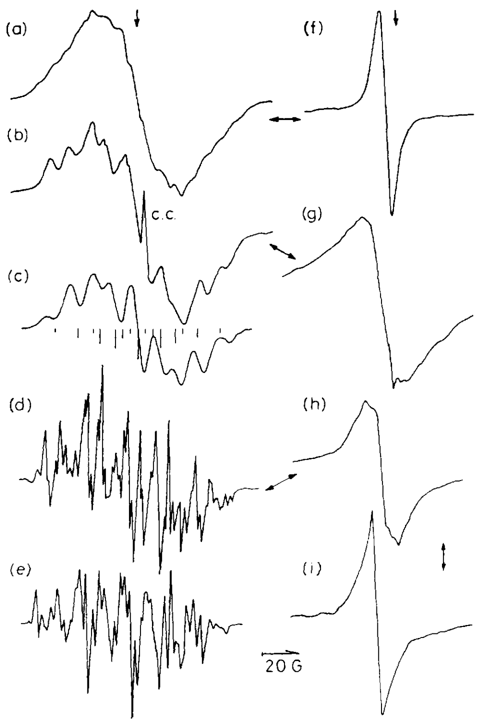


Figure 1. The observed and simulated e.s.r. spectra of cyclo-$C_3H_6^+$. (a) In SF_6 at 4.2 K; (b) in $CFCl_2CF_2Cl$ at 4.2 K; (c) simulation for spectrum (b); (d) in $CFCl_3$ at 4.2 K; (e) simulation for spectrum (d); (f) in SF_6 at 77 K; (g) in $CFCl_2CF_2Cl$ at 77 K; (h) in $CFCl_3$ at 77 K; and (i) in $CFCl_3$ at 140 K. The signal marked 'c.c.' in spectrum (b) is due to a colour centre in the e.s.r. tube. The samples were irradiated at 4.2 K.

unresolvable single-line spectrum (peak-to-peak width, ΔH_{msl}, of *ca.* 15 G) in terms of averaging by dynamic Jahn–Teller effects, since their *ab initio* calculations gave much larger coupling constants for cyclo-$C_3H_6^+$ with static distortion. We have now obtained direct experimental evidence that cyclo-$C_3H_6^+$ possesses a distorted structure at 4.2 K, as is the case with $C_2H_6^+$, and exhibits large and resolvable coupling constants giving a sound basis for the identification of cyclo-$C_3H_6^+$.

As shown in Figure 1(a) and (f), the e.s.r. spectrum of cyclo-$C_3H_6^+$ in SF_6 matrices observed at 4.2 K has an overall width of about 100 G, whereas ΔH_{msl} at 77 K reversibly becomes as narrow as 7.6 G.‡ On the other hand, cyclo-$C_3H_6^+$ in $CFCl_2CF_2Cl$ gives resolvable hyperfine structure at 4.2 K with nearly the same overall width as that in SF_6, Figure (1b), and exhibits a similar narrowing giving a single-line spectrum with $\Delta H_{\text{msl}} = 23$ G at 77 K, Figure 1(g).§ As shown by the spectral simulation in Figure 1(c), the hyperfine structure observed at 4.2 K consists of 5 × 3 lines with 12.5 and 21.0 G couplings to four and two equivalent protons, respectively.

If the symmetrical 3e′ orbital $(\Psi_S)^4$ contains an unpaired electron after loss of an electron, the zeroth order wavefunction suggests a spin density of $\frac{1}{2}$ on both the C-2 and C-3 atoms, providing a reasonable explanation for the observation of four equivalent α-protons attached to C-2 and C-3 as well as the two equivalent β-protons attached to C-1. The observed 12.5 G splitting is consistent with α-proton coupling with a spin density of about a half, whereas the 21.0 G splitting is reasonable for the β-protons with a 60° conformation, if the contributions from both the C-2 and the C-3 atoms are taken into consideration. On the other hand, if the antisymmetric 3e′ orbital $(\Psi_a)^4$ is occupied by an unpaired electron, the 21.0 G splitting must be assigned to α-coupling so that its magnitude may be too large compared with the zeroth order spin density of 2/3 at C-1.

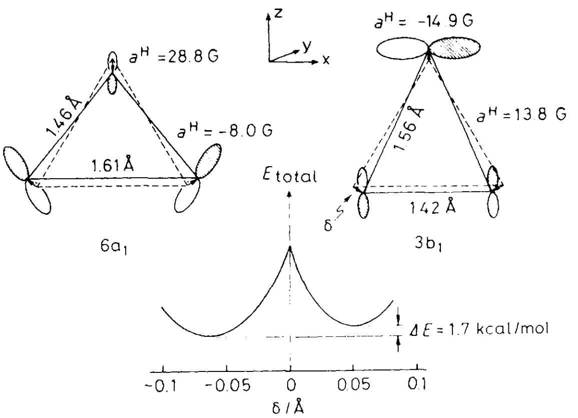
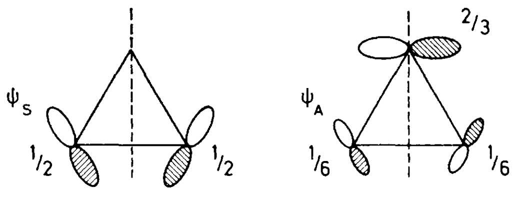


Figure 2. The unpaired electron orbitals and isotropic proton hyperfine coupling constants estimated by the INDO MO method for the two types of distorted structure of cyclo-$C_3H_6^+$ corresponding to the minima of the total energy variation with the distortion, δ, along the e′ ring-deformation normal co-ordinates. The C–C distance before distortion was taken to be 1.51 Å; the C–H distances and H–C–H angles were fixed at 1.089 Å and 115°, respectively.[8]



The Ψ_S orbital is expected to become a singly occupied highest orbital by elongation of the C-2–C-3 bond and shortening of the other bonds because such a deformation reduces the bonding nature of Ψ_S and the antibonding nature of Ψ_a. This is confirmed by INDO MO calculations, the results of which are shown in Figure 2. The calculated coupling constants for Ψ_S are also consistent with the observed values. Thus, it is concluded that the 3e′ orbital in cyclo-C_3H_6 splits into $6a_1$ and $3b_1$ orbitals in cyclo-$C_3H_6^+$ by symmetry reduction from D_{3h} to C_{2v} and the former is occupied by the unpaired electron. Such a distortion is expected from the Jahn–Teller-active e′ ring deformation vibration (ν_{11}),[5,6] as shown in Figure 2.

The marked narrowing of the overall width at elevated temperatures suggest that onset of a dynamic Jahn–Teller effect averages the positive and negative hyperfine couplings. By rapid alternation of the elongated basal C–C bond, each proton becomes a β-proton for one-third of the time giving a positive coupling and an α-proton for two thirds of the time giving a negative coupling. As a result, the averaged coupling becomes as small as $(-12.5 \times 2 + 21.0)/3 = -1.3$ G. This is consistent with the observed small coupling (< *ca.* 2 G) at ⩾ *ca.* 77 K. However, distortion by matrix perturbations and its averaging by rapid rotation around the normal to the

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‡ The cations were radiolytically produced in irradiated frozen solutions[1,3] containing a small amount (0.1—0.5 mol%) of cyclo-C_3H_6.

§ Cyclo-$C_3H_6^+$ in $CFCl_2CF_2Cl$ decomposes at *ca.* 100 K and does not give a narrower single line like that in SF_6.

Table 1. The principal values and directions of the hyperfine and *g*-tensors for cyclo-$C_3H_6^+$ in $CFCl_3$.

		Principal values/G	Dipolar term/G	Direction cosines[a,b]		
				x	y	z
α-H	A_1	−2.8	+8.2	0.578	0.794	0.188
	A_2	−12.3	−1.3	−0.478	0.142	0.868
	A_3	−17.9	−6.9	0.661	−0.592	0.461
	a_{iso}	−11.0 (−12.5)[c]				
β-H	A_1	27.2	+3.2	0.000	0.686	−0.728
	A_2	23.0	−1.0	0.000	0.728	0.686
	A_3	21.8	−2.2	1.000	0.000	0.000
	a_{iso}	24.0 (21.0)[c]				
g	g_{xx}	2.0039		1	0	0
	g_{yy}	2.0060		0	1	0
	g_{zz}	2.0023		0	0	1
	g_{iso}	2.0040 (2.0040)[c]				

[a] The direction cosines are given for one of the protons; those for the others can be obtained by symmetry operations. [b] The *x*, *y*, and *z* co-ordinate system is given in Figure 2. [c] The observed values in $CFCl_2CF_2Cl$,

molecular plane may also account for these observations so that the possibility of matrix effects should not be disregarded.

We have further studied cyclo-$C_3H_6^+$ in $CFCl_3$ at 4.2 K as shown in Figure 1(d). The overall width is nearly the same as that in SF_6 and in $CFCl_2CF_2Cl$, although surprisingly well resolved but complicated hyperfine structures are observed in $CFCl_3$. A similar narrowing of the overall spectral width was also observed at elevated temperatures as shown in Figure 1(h), and (i) ($\Delta H_{msl} = 6.0$ G at 140 K). As shown in Figure 1(e), the essential features of the observed spectrum may be reproduced by simulation¶ using the spin Hamiltonian parameters listed in Table 1. As is expected from the mixing of the nearest lower level, Ψ_a ($3b_1$), the g_{max} direction is perpendicular to the molecular plane.

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¶ The spectral simulations were performed taking the hyperfine and *g* anisotropy as well as the nuclear Zeeman term into consideration. The dipolar tensors were estimated by the method employed by Barfield[7] assuming the following INDO spin densities including negative spins: $\rho_{C\text{-}1}(p_x) = -0.08$, $\rho_{C\text{-}1}(p_z) = 0.09$, $\rho_{C\text{-}2}(p_\sigma) = \rho_{C\text{-}3}(p_\sigma) = 0.46$. The direction of the unpaired electron orbital is assumed to be perpendicular to the HCH plane. The contributions from all the ring spin densities to the dipolar couplings are taken into consideration.