# E.S.R. Evidence for the Static Distortion of $^2E_{1g}$ Benzene Cations giving $^2B_{2g}$ with $D_{2h}$ Symmetry in Low Temperature Matrices†

**Machio Iwasaki,* Kazumi Toriyama, and Keichi Nunome**

*Government Industrial Research Institute, Nagoya, Hirate, Kita, Nagoya 462, Japan*

We have obtained clear e.s.r. evidence that the orbital degeneracy of $^2E_{1g}$ benzene cations is removed at 4.2 K in Freon matrices and the unpaired electron occupies the $b_{2g}$ orbital with $D_{2h}$ symmetry, giving major spin densities on the C(1) and C(4) atoms; however the six carbon atoms become equivalent at >*ca.* 100 K by dynamic averaging.

Recently we have shown that the orbital degeneracy of $^2E_g$ $C_2H_6^+$ is removed by the deformation from $D_{3d}$ to $C_{2h}$ symmetry at 4.2 K in $SF_6$ matrices and that the unpaired electron occupies the $4a_g$ orbital. However, dynamic averaging takes place at 77 K giving the averaged structure with $D_{3d}$ symmetry. The results may be due to static and dynamic Jahn–Teller effects.[1,2] These results stimulated us to examine other typical Jahn–Teller active species at 4.2 K in order to elucidate the distorted structure.

We report herein that the orbital degeneracy of $^2E_{1g}$ $C_6H_6^+$ is also removed at 4.2 K and the unpaired electron occupies the orbital $\Psi_S$ rather than $\Psi_A$ (Figure 1), although dynamic averaging of the unpaired electron distribution takes place at elevated temperatures.

In this work, $C_6H_6^+$ was produced radiolytically in dilute frozen solutions of $C_6H_6$ (0.01—3.0 mol%) in $CFCl_3$, the method developed by Shida and coworkers,[3] and in $CFCl_2CF_2Cl$, the method established by us.[2] The frozen solutions were *X*-irradiated at 4.2 K.

The spectrum of $C_6H_6^+$ in $CFCl_3$ at 4.2 K gives well resolved hyperfine structures [Figure 2(a)], whereas that in $CFCl_2CF_2Cl$ is poorly resolved but has the same overall width and a similar spectral envelope [Figure 2(f)]. At elevated temperatures both spectra show reversible spectral changes, which can be interpreted by dynamic averaging of the hyperfine couplings. The spectrum in $CFCl_2CF_2Cl$ becomes an almost isotropic seven-line spectrum with a binomial intensity ratio at 77—100 K [Figures 2(g) and (h)]. Further warming to 110 K results in an irreversible change into dimer cations giving a familiar thirteen-line spectrum with half splitting[4] [Figure 2 (j)]. On the other hand, dynamic averaging in $CFCl_3$ starts at

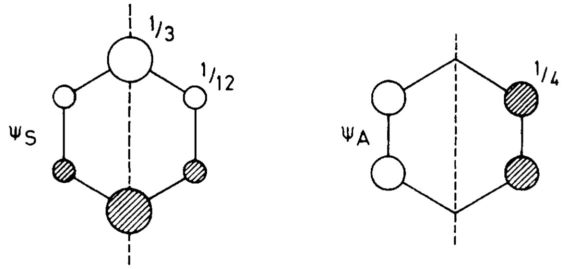

Figure 1

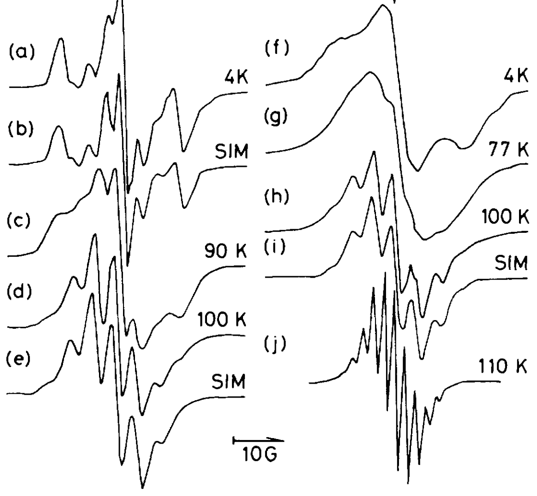

**Figure 2.** The observed and simulated e.s.r. spectra of $C_6H_6^+$: (a)—(e) in $CFCl_3$ and (f)—(j) in $CFCl_2CF_2Cl$. The numbers on the spectra are the temperatures at which they were measured. The spectra marked SIM were simulated using the parameters given in Tables 1 and 2 for (b) and (e), respectively. Spectrum (i) was simulated using the isotropic coupling constant given in Table 1. The solute concentrations were (a) 0.01 mol%; (c), (d) 0.2 mol%; (f)—(h) 0.1 mol%; and (i) 0.5 mol%. The samples were *X*-irradiated at 4.2 K.

---

† The preliminary results were presented as a part of our report on alkane cations at the 46th Autumn Annual Meeting of CSJ, Niigata, October 3, 1982 (Abstract p. 13) and at the 21st ESR Symposium, Tsukuba, October 26, 1982 (Abstract p. 48).

**Table 1.** Principal values and directions for the hyperfine and $g$ tensors of $C_6H_6^+$ with the $b_{2g}$ S.O.M.O. trapped in $CFCl_3$ at 4.2 K.

| | Hyperfine and $g$ tensors/G | | Observed dipolar term/G | Calculated dipolar term/G[b] | Principal direction |
|---|---|---|---|---|---|
| 1-H, 4-H | $A_1$ | −3.7 | +4.5 | +5.1 | ∥ C–H |
| | $A_2$ | −13.3 | −5.1 | −4.6 | ⊥ C–H in plane |
| | $A_3$ | −7.6 | −0.6 | −0.6 | ⊥ Molecular plane |
| | $a_{iso}$ | −8.2 (−9.45)[a] | | | |
| 2-H, 3-H<br>5-H, 6-H | $A_1$ | −3.6 | −1.2 | −1.5 | −4° from C–H |
| | $A_2$ | 0.0 | +2.4 | +2.6 | 86° from C–H |
| | $A_3$ | −3.6 | −1.2 | −1.1 | ⊥ Molecular plane |
| | $a_{iso}$ | −2.4 (−1.20)[a] | | | |
| $g$ | $g_1$ | 2.0029 | | | ∥ C(1)–C(4) |
| | $g_2$ | 2.0029 | | | ⊥ C(1)–C(4) |
| | $g_3$ | 2.0023 | | | ⊥ Molecular plane |
| | $g_0$ | 2.0027 | | | |

[a] The numbers in parentheses are the isotropic hyperfine coupling constants obtained from INDO M.O. calculations assuming $r$[C(1)–C(2)] = 1.452 Å and $r$[C(2)–C(3)] = 1.387 Å with $D_{2h}$. [b] $\rho$[C(1)] = 1/3 and $\rho$[C(2)] = 1/12 are assumed (see text).

*ca.* 90 K [Figure 2(c)] and the spectrum is slightly asymmetric even at 100 K [Figure 2(d)]. The hyperfine coupling constant of 4.32 G obtained from both matrices at elevated temperatures agrees with a literature value of 4.4 G for $C_6H_6^+$ on silica gels.[4] It is to be noted here that the spectra of $C_6H_6^+$ in $CFCl_3$ often exhibit a marked orientational effect as shown in Figure 3.‡

The spectrum in $CFCl_3$ at 4.2 K clearly indicates that the six protons of $C_6H_6^+$ are inequivalent and exhibit hyperfine and $g$ anisotropy. The spectrum can be simulated by the spin distribution expected from the $\Psi_S$ orbital as shown in Figure 2(b) using the spin Hamiltonian parameters listed in Table 1.§ In this simulation the sum of the isotropic coupling constants is taken to be equal to that in the isotropic spectrum at elevated temperatures, *i.e.* 25.9 G. The spin densities on C(1) and C(2) are estimated to be 0.32 and 0.09, respectively, from the observed isotropic coupling constants using $Q_{CH}$ 25.9 G. These values are approximately equal to those expected from the Hückel M.O. coefficients for $\Psi_S$. The dipolar tensors are in reasonable agreement with the calculated tensors¶ as shown in Table 1.

Although the removal of orbital degeneracy by matrix perturbations and their averaging out at elevated temperature might account for these observations, the distortion due to the Jahn–Teller instability must play an important role at least as a driving force in the molecular distortion.

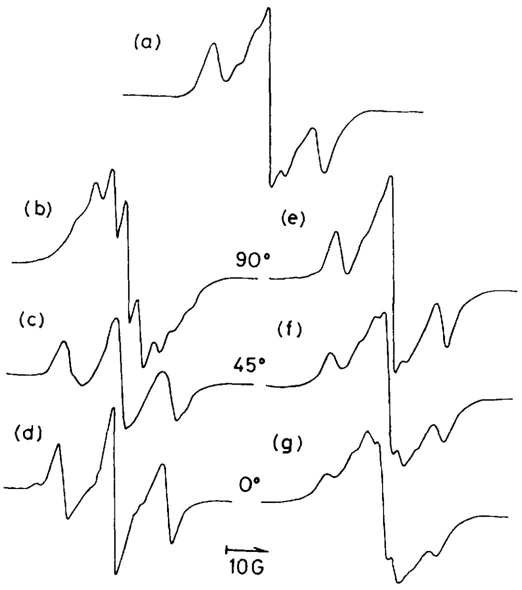

**Figure 3.** Powder and oriented spectra of $C_6H_6^+$ in $CFCl_3$ measured at 77 K. (a) Powdered samples; (b)—(d) oriented samples in which the molecular plane of $C_6H_6^+$ is preferentially aligned parallel to the tube axis; and (e)—(g) oriented samples in which the molecular plane of $C_6H_6^+$ is preferentially aligned perpendicular to the tube axis. The magnetic field is applied (b), (e) perpendicular; (c), (f) along 45°; and (d), (g) parallel to the tube axis. The samples were γ-irradiated at 77 K. The solute concentrations are (a) 0.2 mol%; (b)—(d) 0.01 mol%; and (e)—(g) 3 mol%.

Among the four $e_{2g}$ modes, which are Jahn–Teller active,[8] the degenerate C–C stretching and the degenerate C–C–C bending modes lead to ring deformation which reduces the molecular symmetry from $D_{6h}$ to $D_{2h}$. Since the shortening of the C(2)–C(3)[C(5)–C(6)] bond increases the antibonding nature of $\Psi_S$ and the lengthening of other C–C bonds decreases the bonding nature, $\Psi_S$ is expected to become a singly occupied molecular orbital ($b_{2g}$ with $D_{2h}$) by such distortion. This expectation is confirmed by INDO M.O. calculations. Although complete geometry optimization was not performed, the deformation mentioned above along the $e_{2g}$ degenerate C–C stretching mode leads to the $b_{2g}$ S.O.M.O. giving isotropic coupling constants of −9.45 G and −1.20 G

---

‡ After completion of this work, we have become aware of work on a new type of benzene dimer cation reported by Shida and co-workers.[5] At 77 K they have observed a seven-line (correctly nine-line) spectrum similar to that shown in Figure 3(b) for samples with low solute concentrations (<*ca.* 0.2 mol%) and a three-line spectrum similar to that shown in Figure 3(e) for samples with relatively high solute concentrations (1—5 mol%). They have attributed the former to monomer cations and the latter to dimer cations with a perpendicular configuration, which removes the orbital degeneracy stabilizing the $\Psi_S$ orbital. It would appear that the solute concentration affects the preferential orientation of $C_6H_6$ in $CFCl_3$.

§ As the anisotropic hyperfine couplings were close to or less than 10 G, the inclusion of the nuclear Zeeman term for all the protons was necessary in order to obtain a proper lineshape.

¶ The typical α proton coupling tensor (+12.8, −12.8, 0) G[6] is combined with the contributions from the neighbouring spins using the two centred integrals given by Barfield.[7]

**Table 2.** Observed hyperfine coupling constant and $g$ value at 100 K in $CFCl_2CF_2Cl$ and the dynamically averaged principal values of hyperfine and $g$ tensors obtained from the rigid tensors at 4.2 K in $CFCl_3$.

| Observed $a_{iso}$/G | Averaged hyperfine tensor/G | Observed $g_0$ value | Averaged $g$ tensor | Principal direction |
|---|---|---|---|---|
| | $A_\perp$ −4.0 | | $g_\perp$ 2.0029 | in plane |
| | $A_\parallel$ −4.9 | | $g_\parallel$ 2.0023 | ⊥ plane |
| −4.32 | $a_{iso}$ −4.3 | 2.0028 | $g_0$ 2.0027 | |

with $\rho$[C(1)] 0.430 and $\rho$[C(2)] 0.035.** These values are in reasonable agreement with those observed (see Table 1).

On considering the $g$ anisotropy, $C_6H_6^+$ with $\Psi_S(1e_{1g})$ is expected to exhibit a positive $g$ shift in the molecular plane owing to the excitation from the nearest lower $\sigma_{CC}$ and $\sigma_{CH}$ orbitals ($3e_{2g}$), and a free spin $g$ value along the normal to the molecular plane. The observed $g$ tensor given in Table 1 is consistent with this expectation.

We suggest that dynamic averaging takes place by rapidly alternating the three equivalent distorted structures. In such a case, the averaged hyperfine and $g$ tensors must have axial anisotropy with respect to the normal to the molecular plane as shown in Table 2. Although the hyperfine tensor becomes almost isotropic, the residual $g$ anisotropy gives an asymmetric spectrum as shown in Figures 2(d) and 2(e). A more symmetrical spectrum in $CFCl_2CF_2Cl$ at 100 K may be due to a higher molecular mobility in the glassy matrices.

*Received, 6th December 1982; Com. 1400*

## References

1 M. Iwasaki, K. Toriyama, and K. Nunome, *J. Am. Chem. Soc.*, 1981, **103**, 3591; K. Toriyama, M. Iwasaki, and K. Nunome, *J. Chem. Phys.*, 1983, **77**, 5891.

2 K. Toriyama, K. Nunome, and M. Iwasaki, *J. Phys. Chem.*, 1981, **85**, 2149.

3 T. Shida, Y. Egawa, and H. Kubodera, *J. Chem. Phys.*, 1980, **73**, 5963 and references cited therein.

4 O. Edlund, P. O. Kinell, A. Lund, and A. Shimizu, *J. Chem. Phys.*, 1967, **46**, 3679.

5 M. Shirakawa, T. Shida, Y. Nosaka, and M. Imamura, Symposium on Molecular Structures, Fukuoka, October 1980, Abstract p. 176.

6 W. Gordy, 'Theory and Applications of Electron Spin Resonance,' Wiley, New York, 1980, p. 215.

7 M. Barfield, *J. Chem. Phys.*, 1970, **53**, 3836; 1971, **55**, 4682.

8 G. Herzberg, 'Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules,' Van Nostrand Reinhold, New York, 1966, p. 50.

---

** The carbon spin densities are considerably larger than those expected from the coefficients of the wave function owing to the spin polarization effect. The squares of the coefficients are 0.368 and 0.066 for C(1) and C(2) atoms, respectively.