Electron Spin Resonance Study of Electronic and Geometrical Structures of $C_2H_6^+$ and Other Simple Alkane Cations at 4.2 K: Possible Evidence for Jahn–Teller Distortion

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ESR observations of simple alkane cations such as CH_4^+, $C_2H_6^+$, etc., have long been a matter of concern because of a strong interest in their geometrical and electronic structures as well as their role in radiolysis of alkanes. Nevertheless, the ESR detection of simple alkane cations has not been successful, and they have long been believed to be quite unstable and to decompose into neutral radicals by proton loss.

In the present paper we wish to report the ESR characterization of $C_2H_6^+$, $C_3H_8^+$, *i*-$C_4H_{10}^+$, and *neo*-$C_5H_{12}^+$ trapped in SF_6 and other matrices at 4.2 K. Our results may shed light on the electronic and geometrical structures of simple alkane cations as well as alkanes themselves, which have not been well elucidated.[1,2] Information on the Jahn–Teller distorted structure and the unpaired electron distributions determined from our ESR study should be useful for further theoretical studies on the structures of such prototype compounds.

Gaseous mixtures of SF_6 and alkanes (0.5–1 mol%) were frozen into an ESR tube at 4.2 K. They were irradiated at 4.2 K by X-rays (45 kV, 40 mA) for 15 min, and then ESR spectra were measured at 4.2 K without transferring the sample.[3,4] An electron ejected by the ionizing radiation is captured by SF_6 forming SF_6^- which gives a background spectrum widely spread over 1500 G because of large anisotropic fluorine hyperfine couplings.[5] On the other hand, the positive charge transfer takes place from the matrices to the alkanes, because the ionization potentials of the alkanes are considerably lower than that of SF_6 with IP = 15.69 eV.[6] Halocarbon matrices such as CCl_4 and CCl_3F are often used to stabilize cationic species,[7,8] but $C_2H_6^+$ could not be well identified in these matrices.

As shown in Figure 1 and Table I, even at 4.2 K all the cations studied exhibit simple isotropic hyperfine structures which can be ascribable to the 1s spin density on the hydrogen atoms in the C–H bonds. After second-order corrections were made, the *g* values of these cations were found to be 2.002–2.003. The spectrum obtained from $C_2H_6^+$ exhibits a 1:2:1 three-line hyperfine structure with an extremely large splitting of 152 G at 4.2 K (Figure 1a). Such a large splitting is not expected from neutral radicals but is expected from an unpaired electron in the MO confined to the two C–H σ bonds in $C_2H_6^+$, that is, the $1e_{gx}$ orbital shown in Figure 2a.[9] It is clear that 60% of the total spin density is confined to two hydrogen 1s orbitals. Judging from the line width, the hyperfine coupling with the remaining protons is less than 10 G so that the spin density on the remaining four hydrogen atoms is less than 0.08.

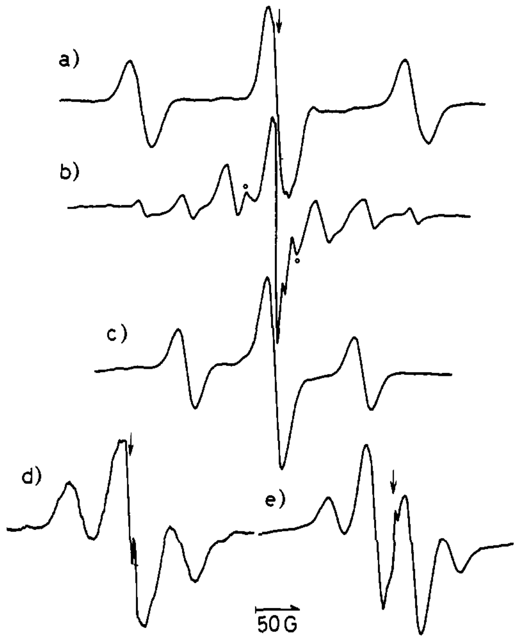


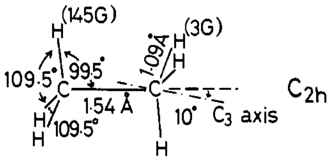
Figure 1. ESR spectra of (a) $C_2H_6^+$ measured at 4.2 K, (b) $C_2H_6^+$ at 77 K, (c) $C_3H_8^+$ at 4.2 K, (d) *i*-$C_4H_{10}^+$ at 4.2 K and (e) *neo*-$C_5H_{12}^+$ at 4.2 K. The matrices are SF_6 for (a)–(d), and CCl_3F for (e). The weak overlapping spectrum from SF_6^- is subtracted for (a) and (d). The signals marked with a circle in (b) are the central part of the C_2H_5 spectrum. The arrows indicate the position of the DPPH marker.

Table I. Proton Hyperfine Coupling Constant (a_H), 1s Spin Density on Hydrogen Atoms (ρ_H), Highest Occupied Molecular Orbital (HOMO), and Jahn–Teller (JT) Lowering of Symmetry for Alkane Cations

cations	a_H (4.2 K), G	$\Sigma\rho_H{}^a$	HOMO	JT distortion
$C_2H_6^+$	152 (2 H)	0.60	$1e_{gx}$	$D_{3d} \rightarrow C_{2h}$
$C_3H_8^+$	98 (2 H)	0.39	$4b_1$	C_{2v}
i-$C_4H_{10}^+$	53 (2 H)	0.21	5e	$C_{3v} \rightarrow C_s$
neo-$C_5H_{12}^+$	42 (3 H)	0.25	$4t_2$	$T_d \rightarrow C_{3v}$

[a] Sum of the spin densities on H 1s orbitals is simply estimated by assuming a_H = 508 G for ρ = 1.

Our INDO calculations show that $C_2H_6^+$ with the same geometry as C_2H_6 (D_{3d}) indeed has the unpaired electron in the $1e_{gx}$ orbital, giving a splitting of 140 G for the two in-plane protons (2 H) and 35 G for the four out-of-plane protons (4 H). A slight deformation (10°) from D_{3d} to C_{2h} with the following geometry results in 145 G for 2 H and 3 G for 4 H in agreement with the observation. The results suggest that the electronic degeneracy of $C_2H_6^+$ in the ^2E state is removed by lowering the symmetry from D_{3d} to C_{2h} by Jahn–Teller effect, although a possibility of deformation due to matrix effects cannot be completely excluded. The vibronic coupling mode is probably the Jahn–Teller active e_g CH_3 rocking vibration (ν_{12}).[1c,10,11] The INDO calculation shows



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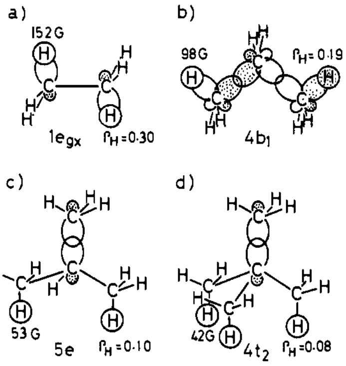

Figure 2. Unpaired electron orbitals of (a) $C_2H_6^+$, (b) $C_3H_8^+$, (c) *i*-$C_4H_{10}^+$, and (d) *neo*-$C_5H_{12}^+$.

that the observed spin density cannot be expected from the deformation associated with the Jahn–Teller active e_g CH_3 deformation vibration (ν_{11}).

When the spectrum is measured at 77 K, the three-line spectrum changes reversibly into an equally spaced seven-line spectrum with a 50.4-G splitting and a total spread unchanged from that of the 4.2-K spectrum (Figure 1b). This indicates the onset of motion, driven by a dynamic Jahn–Teller effect. Upon further warming, $C_2H_6^+$ converts into a neutral C_2H_5 radical, giving strong evidence for our assignment to $C_2H_6^+$.

The spectrum of $C_3H_8^+$ arises from two equivalent protons with coupling constants of 98 G (Figure 1c); this indicates that the $4b_1$ orbital (Figure 2b) is the highest occupied level of C_3H_8 (C_{2v}),[2] because the other orbitals, such as $6a_1$, $2b_2$ cannot give a large spin density (0.39) only on the two equivalent protons, as is observed. Upon warming, $C_3H_8^+$ loses a proton and converts into $\dot{C}H_2CH_2CH_3$ and $CH_3\dot{C}HCH_3$, the former being predominant as is expected from the spin distribution in $C_3H_8^+$.

The a_1 and a_2 orbitals of *i*-C_4H_{10} (C_{3v}) cannot give two equivalent proton couplings (53 G) as is observed (Figure 1d); so the Jahn–Teller split 5e orbital must be the highest occupied level.[2] The relatively small hyperfine coupling of *i*-$C_4H_{10}^+$ suggests that the unpaired electron is considerably localized in one of three C–C σ bonds as a result of Jahn–Teller distortion from C_{3v} to C_s symmetry. The hyperfine splitting of 53 G can be expected from the β protons in the two C–H bonds which are trans to the C–C σ-unpaired orbital as shown in Figure 2c. However, the possibility of the antibonding combination of the two C–C bonding orbitals similar to $4b_1$ in $C_3H_8^+$ cannot be excluded. Upon warming, *i*-$C_4H_{10}^+$ in SF_6 matrices converts into $\dot{C}H_2CH(CH_3)_2$ and $\dot{C}(CH_3)_3$ by proton loss, the former being predominant as is expected.

The highest occupied orbital of *neo*-C_5H_{12} (T_d) is $4t_2$.[2] *neo*-$C_5H_{12}^+$ has three equivalent protons with 42-G couplings (Figure 1e); this suggests that the unpaired electron is localized in one of the four C–C bonds as a result of Jahn–Teller distortion from T_d to C_{3v}. The $4t_2$ level of the parent molecule with T_d symmetry splits into a_1 and e states in the cation with C_{3v} symmetry, and the former is mainly confined to the C–C σ bond (Figure 2d). The 42-G coupling can be expected from the β protons (trans), one each from the three methyl groups as shown in Figure 2d. Upon warming, *neo*-$C_5H_{12}^+$ in SF_6 converts into $\dot{C}H_2C(CH_3)_3$ by proton loss while that in CCl_3F converts into $CH_2{=}C(CH_3)_2^+$ by loss of CH_4.[12] The difference may be due to cage effects in more rigid matrices.

In conclusion, small *n*-alkanes give C–H σ cations, and the spin density in the C–H σ bonds decreases with increasing carbon numbers. In branched alkanes the unpaired electron is more confined to the C–C σ bond.

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Hybrid Multidentate Ligands. Tridentate Amidophosphine Complexes of Nickel(II) and Palladium(II)

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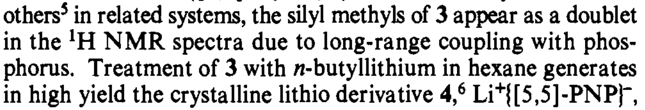
We have initiated a synthetic program to explore the coordination chemistry of a new class of potentially multidentate ligands which we call "hybrid" ligands. These hybrid ligands combine the *hard*[1] donor amido ligand (amido ≡ NR_2^-; R = alkyl, aryl, or silyl) with suitable *soft* donors such as phosphines, arsines, olefins, thioethers, or isocyanides into a chelating array. Our strategy is to take advantage of the chelate effect[2] to insure multidenticity in hybrid ligands of the types shown in Figure 1.

The tridentate hybrid ligand **1** can be formally classified as a *uninegative* six-electron donor (cf. η^5-$C_5H_5^-$ and η^5-$C_5Me_5^-$), while **2** would be similarly classified as a *uninegative* four-electron donor (cf. η^3-$C_3H_5^-$). It is anticipated that these hybrid ligands will induce new reactivity in their transition-metal derivatives over that observed in derivatives of the component monodentate donors. We report here some preliminary work with a potentially tridentate ligand of the type **1** where L is a tertiary phosphine.

The synthesis of 1,3-bis[(diphenylphosphino)methyl]tetramethyldisilazane, $(Ph_2PCH_2SiMe_2)_2NH$ (**3**), follows straightforward procedures.[3a,4] We classify this ligand as belonging to the set of *neutral*, potentially tridentate chelates represented by the nomenclature {[5,5]-P(NH)P}.[3b] As noted by Schore and others[5] in related systems, the silyl methyls of **3** appear as a doublet in the ^1H NMR spectra due to long-range coupling with phosphorus. Treatment of **3** with *n*-butyllithium in hexane generates in high yield the crystalline lithio derivative **4**,[6] $Li^+\{[5,5]\text{-PNP}\}^-$, which is a convenient starting material for metathetical reactions with a variety of suitable transition-metal halide derivatives, in analogy to other work with monodentate amido precursors.[7-9]



3 **4** (1)

The reaction of **4** with $NiCl_2(PR_3)_2$ (R = Ph[10a] or Me[10b]) in

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[4] **3**: colorless needles from pentane, mp 45–46 °C; ^1H NMR (ppm, C_6D_6, 60 MHz) 0.10 (d, 12, $SiCH_3$, J = 1.0 Hz), 1.36 (d, 4, PCH_2, J < 1 Hz), phenyl region not listed. Anal. Calcd for $C_{30}H_{37}NSi_2P_2$: C, 68.05; H, 6.99; N, 2.65. Found: C, 68.33; H, 7.25; N, 2.55.

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[6] **4**: colorless plates from toluene–hexane, mp 120 °C dec; ^1H NMR (ppm, C_6D_6, 60 MHz) –0.05 (br s, 12, $SiCH_3$), 1.58 (br s, 4, PCH_2), phenyl region not listed. Anal. Calcd for $C_{30}H_{36}LiNSi_2P_2$: C, 67.29; H, 6.73; N, 2.61. Found: C, 67.00; H, 6.78; N, 2.48.

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