Table I. Hyperfine Coupling Constants of $H_2PC1^{\bullet-}$

	hfc [MHz] sodium reductn[a]	hfc [MHz] electrolysis[b]	hfc [MHz] simulation and least-squares fit[c]
H			
a_1	+0.53 ± 0.03	+0.51 ± 0.03	0.50
a_2	−2.65	−2.68	2.63
a_3	−4.10	−4.10	4.04
a_4	−5.05	−5.03	5.07
N			
a_N	−2.00	−2.00	2.05

[a] Experimental conditions: For H-ENDOR: T = 193 K, mw power 5 mW, rf power 75 W, 10 kHz fm of rf field, ±40 kHz deviation, no field modulation, time constant 0.4 s, 6 scans. For ^{14}N-ENDOR: T = 254 K, mw power 5 mW, rf power 150 W, 10 kHz fm of rf field, ±50 kHz deviation, 1 kHz magnetic field modulation, time constant 0.4 s, 6 scans. [b] Experimental conditions: For H-ENDOR: rf power 60 W, 5 scans. For ^{14}N-ENDOR: T = 193 K, rf power 100 W, 4 scans. The other conditions are similar to those in note a. [c] Component Lorentz line of 43 mG width, number of iterations 1000.

The optical spectrum of partially reduced H_2PC1 in THF was found to be similar to that of the neutral species except for two new bands appearing at 524 and 426 nm. Cyclic voltammetry measurements of H_2PC1 in THF/TBAP demonstrate that the first reduction step is a reversible one-electron process. The ESR spectrum of chemically reduced H_2PC1 in THF at 240 K (g value of 2.0025) is depicted in Figure 2a. Unlike the ESR spectra of the anion radicals of free-base porphyrins, which do not exhibit any hyperfine structure,[10,11] the ESR spectrum of $H_2PC1^{\bullet-}$ is highly resolved. This difference in spectral resolution is attributed to two effects: First, the hfc's of the H_2PC1 anion are approximately integer multiples of the smallest hfc, a_1 (see Table I). Consequently, accidental ESR line degeneracy occurs which drastically reduces the number of lines in the spectrum. Secondly the lack of hyperfine structure in the ESR spectra of porphyrin anions with unperturbed D_{4h} symmetry is attributed to Jahn–Teller line broadening due to orbital degeneracy.[12] The reduced symmetry of porphycene (D_{2h} instead of D_{4h}) is expected to lift the orbital degeneracy leading to much smaller line widths.

An ENDOR spectrum of $H_2PC1^{\bullet-}$ is presented in Figure 2b. For a doublet radical in solution two ENDOR lines per hfc, a_{iso}, are expected at frequencies

$$\nu^{\pm}_{\mathrm{ENDOR}} = |\nu_n \pm a_{\mathrm{iso}}/2|$$

where $\nu_n = (g_n\mu_K/h)B$ is the nuclear Larmor frequency.[8] The proton-ENDOR spectrum of $H_2PC1^{\bullet-}$ reveals four pairs of lines symmetrically arranged around ν_H = 14.38 MHz. The corresponding H-hfc's are listed in Table I, both for chemically and electrolytically generated $H_2PC1^{\bullet-}$. At 2.04 MHz one ^{14}N-line was detected. The ^{14}N Larmor frequency was calculated to be 1.04 MHz. Thus, the corresponding low-frequency line is expected at 0.04 MHz which is below the frequency range of the spectrometer. The relative signs of the H-hfc's and the ^{14}N-hfc could be determined by "General TRIPLE" experiments.[8,13] The absolute signs of the hfc's given in Table I are based on the assumption that the largest H-hfc, a_4 = 5.05 MHz (±30 kHz), is negative.[14]

The spectra of chemically and electrolytically generated $H_2PC1^{\bullet-}$ are identical within experimental error. This, together with the results from optical spectroscopy and cyclic voltammetry, confirms the identity of the investigated radical.

In order to assign the hfc's to the different positions in the molecule, the $H_2PC1^{\bullet-}$ ENDOR spectrum was compared with the ENDOR spectra of $H_2PC2^{\bullet-}$, $H_2PC3^{\bullet-}$, and $PdPC2^{\bullet-}$. The smallest H-hfc is equal for $H_2PC1^{\bullet-}$ and $H_2PC2^{\bullet-}$, whereas it is missing for $PdPC2^{\bullet-}$. Therefore, a_1 must be attributed to the two (N-H) protons of H_2PC1. Similarly, the second smallest hfc is equal for $H_2PC1^{\bullet-}$ and $H_2PC2^{\bullet-}$, whereas it is missing for $H_2PC3^{\bullet-}$. Consequently, a_2 is assigned to the set of four equivalent protons at the positions 9, 10, 19, and 20. For the other two sets of four equivalent protons at the pyrrole rings an assignment has not yet been made.

The ESR spectrum was simulated with the hfc's obtained from ENDOR, the respective number of equivalent protons being chosen according to the aforementioned assignment. The simulation was found to be in very good agreement with the experimental spectrum provided that four nitrogens were attributed to the measured N-hfc. This indicates that, on the ESR time scale and within the experimental resolution, all four nitrogens are equivalent.[15] The simulated ESR spectrum was also fitted to the experimental ESR spectrum with an iterative least-squares fit program.[16] The resulting slightly modified hfc's are listed in the last column of Table I.

Theoretical studies using an all-valence electron SCF MO method[17] will be performed in due course in order to interpret the spectroscopic results and gain information on the electronic structure of doublet state porphycenes.

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ESR Evidence for the $^2A_1$ State of the Hexamethyl (Dewar) Benzene Radical Cation

Christopher J. Rhodes

School of Chemistry, Thames Polytechnic
Wellington Street, Woolwich
London, SE18 6PF, England

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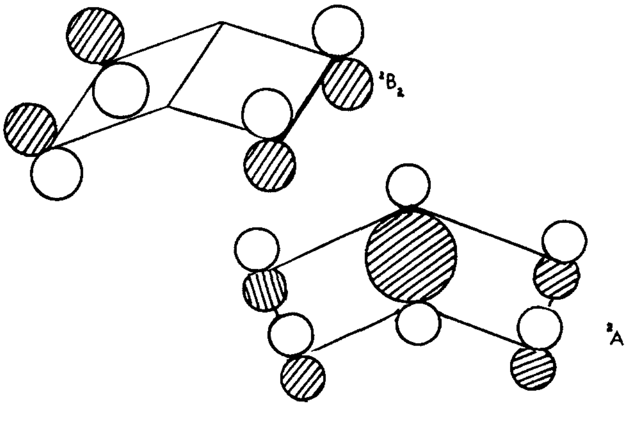
In a recent communication[1] we reported an ESR observation of hexamethyl (Dewar) benzene (HMD) radical cations, following γ-irradiation of the parent compound as a dilute frozen solution in $CFCl_3$ at 77 K. The ESR results showed that the unpaired electron was coupled to the protons of four equivalent methyl groups, and so the cation was identified as existing in the $^2B_2$ state.



On warming the sample from 77 K, an abrupt, irreversible change

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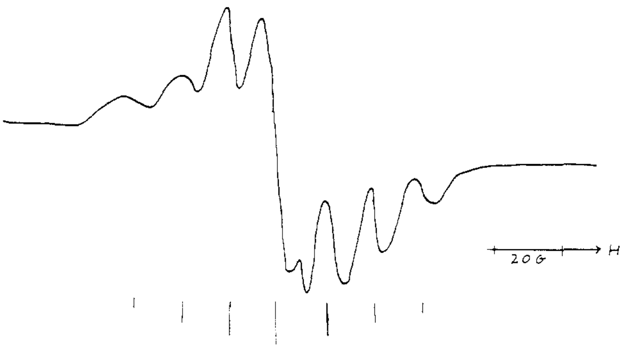
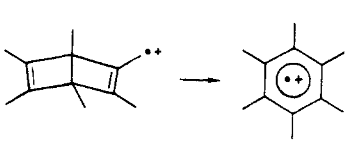


Figure 1. X-band ESR spectrum recorded following γ-irradiation of hexamethyl (Dewar) benzene in $CFCl_2CF_2Cl$ at 77 K, showing features assigned to ($^2A_1$) $HMD^{\bullet+}$ radical cations.

occurred in the spectrum, which became identical with that observed from authentic hexamethylbenzene (HMB) under the same conditions. Therefore, the ring-opening reaction 1 must have



(1)

occurred: this is known to take place extremely rapidly in the liquid phase at higher temperatures.[2] We suggested that, at 77 K, the $CFCl_3$ molecules pack sufficiently rigidly around the HMD molecules to prevent the reaction 1 taking place following ionization.

In order to examine the effect of the matrix material on the properties of the $HMD^{\bullet+}$ cation, we repeated these experiments with $CFCl_2CF_2Cl$ in place of $CFCl_3$. The resulting ESR spectrum (Figure 1) is completely different and appears to comprise of seven lines, which is consistent with a SOMO involving two equivalent methyl groups [A(H) = 14 G]. We interpret this as being due to the $^2A_1$ form of the $HMD^{\bullet+}$ cation, in which the unpaired electron is largely confined to the ("stretched") transannular C–C bond. A recent MINDO/3 calculation has predicted that the minimum energy geometry for the parent (Dewar) benzene radical cation does possess an elongated transannular bond,[3] which, taken with the ESR result suggests that the $^2A_1$ state is more stable than the energetically similar $^2B_2$ state; however, we note that ab initio calculations predict the $^2B_2$ state to be the more stable by 8 kcal/mol.[4] The polarization observed in a photo-CIDNP study of HMD with excited (triplet) electron acceptors gave evidence for the formation of both states, proposed to arise via competing pathways.[4]

On annealing the sample, an irreversible change occurred in the ESR spectrum, similar to that observed in the $CFCl_3$ matrix: the resulting spectrum (Figure 2) containing features due to ring-opened ($HMB^{\bullet+}$) radical cations [A(H) = 6.7 G]. This strongly supports our assignment of the initial seven line spectrum (Figure 1) as arising from *a different electronic state* of the *same* $HMD^{\bullet+}$ cation.

We tentatively suggest that the difference between the two matrices may be due to a less rigid structure for solid $CFCl_2CF_2Cl$ which can permit the $HMD^{\bullet+}$ framework to relax via stretching of the transannular C–C bond. This appears to be a remarkable demonstration that the structure adopted by a radical cation can be determined by the nature of the matrix material in which it is isolated;[8] hence, we suggest that the more tightly packed $CFCl_3$ matrix hinders the significant elongation of the central C–C bond required for the formation of the $^2A_1$ structure and the alternative $^2B_2$ state is formed.[5]

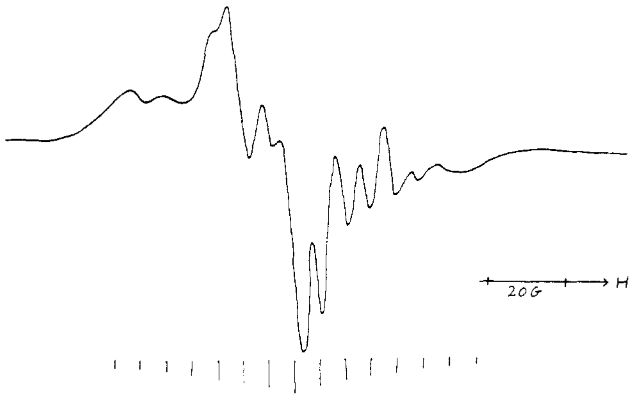


Figure 2. X-band ESR spectrum recorded following annealing of the $CFCl_2CF_2Cl$ matrix containing $HMD^{\bullet+}$ radical cations, assigned to $HMB^{\bullet+}$ radical cations formed by ring opening.

We consider that it is possible that lesser amounts of the $^2B_2$ form may be present along with the $^2A_1$ form in the $CFCl_2CF_2Cl$ matrix; however, the $^2A_1$ form clearly dominates, in contrast with the results in $CFCl_3$.

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Substitution Competes with Elimination in a Gas-Phase Anion-Molecule Reaction

Rachel C. Lum and Joseph J. Grabowski*

Department of Chemistry, Harvard University
12 Oxford Street, Cambridge, Massachusetts 02138

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In ethanol solution, ethoxide reacts with propyl bromide to predominantly produce products from substitution; only 8.8% of the reaction proceeds by elimination.[1] However the few studies carried out in the gas phase, which compare substitution to elimination pathways for anion-molecule reactions, indicate that elimination is kinetically preferred over substitution, even when both channels are considerably exothermic.[2] We wish to report that for the strong base amide, interacting with ethylmethyl sulfite in the gas phase, substitution and elimination reactions at saturated carbon are nearly equally favored.

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