racyanoethylene are hydrogenated using $RuHCl(PPh_3)_3$, the reaction solutions change color rapidly, the Ru–H resonance disappears within 15 s, and hydrogenation is observed after 15 min, but no PHIP is detected.

While the present study does not resolve the complexities of the $RuHCl(PPh_3)_3$ catalyst system, it does show that a pairwise hydrogen transfer pathway exists, most probably via $RuH_2(PPh_3)_3$. In addition, the change in polarization with change in substrate using $RuH_4(PPh_3)_3$ in C_6D_6 suggests that PHIP may be useful in establishing relative rates. This aspect is under continuing study.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE 86-05033) for support of this work, the Johnson Matthey Co., Inc. for a generous loan on ruthenium salts, and Prof. Alan Stolzenberg and Prof. Brian James for helpful discussions.

Registry No. $RuH_4(PPh_3)_3$, 31275-06-6; $RuHCl(PPh_3)_3$, 55102-19-7; ethylene-d_4, 683-73-8; styrene-d_8, 19361-62-7; phenylacetylene, 536-74-3; methyl acrylate, 96-33-3.

Anion Radicals of Porphycenes: First ESR and ENDOR Characterization

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Received July 11, 1988

It has been established that porphyrinoid systems are essential chromophores in many photochemical and photobiological processes. This includes a new class of porphyrin isomers, named porphycenes (Figure 1), which have been recently synthesized and characterized.[1,2] Investigations of their role in photophysical and photochemical processes have been started.[3-5] The difference in molecular design and symmetry between porphyrins and porphycenes leads to different spectroscopic behavior as found in recent studies on the photoexcited singlet and triplet states.[3-5] The doublet state radical ions of porphycenes should also be of considerable interest in comparison with those of analogous porphyrins in view of anticipated relationships between electronic structure and reactivity of these compounds.

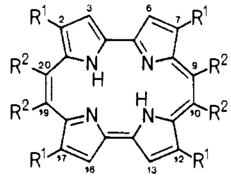

Figure 1. Porphycenes; D_{2h} symmetry on the ESR and NMR time scale: H_2PC1 (parent compound), $R_1 = R_2 = H$; H_2PC2, $R_1 = C_3H_7$, $R_2 = H$; H_2PC3, $R_1 = H$, $R_2 = C_3H_7$; PdPC2, the two central H's are replaced by Pd, $R_1 = C_3H_7$, $R_2 = H$.

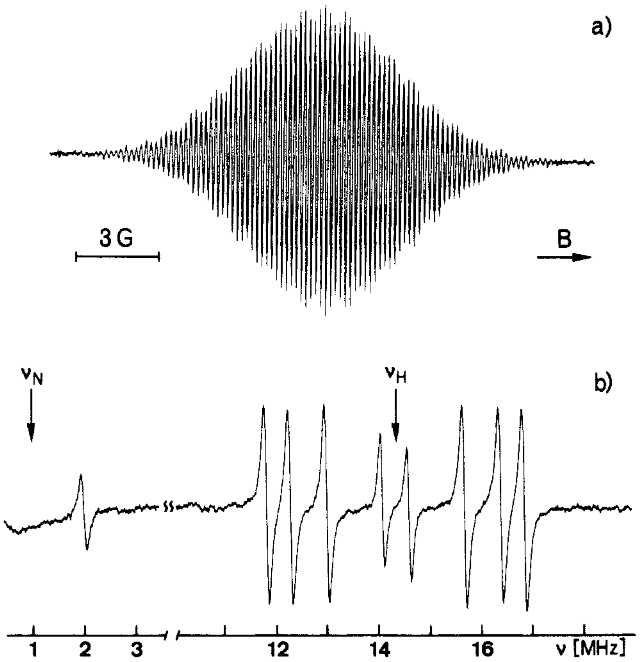

Figure 2. (a) ESR spectrum of $H_2PC1^{\bullet-}$ in THF at 240 K. (b) ^{14}N- and H-ENDOR spectrum of $H_2PC1^{\bullet-}$ in THF at 193 K; experimental conditions: see note b of Table I.

In this communication we report on liquid phase ESR, electron nuclear double resonance (ENDOR), and electron nuclear nuclear triple resonance (TRIPLE) measurements of isotropic interaction parameters such as g factor and H- and ^{14}N-hyperfine coupling constants (hfc's) of the unsubstituted free-base porphycene (H_2PC1) anion radical. An extended study on the other porphycenes shown in Figure 1 will be presented in a forthcoming publication.

The anion radicals of the porphycenes were prepared chemically by reduction with sodium metal under high vacuum conditions.[6] Tetrahydrofuran (THF) was used as a solvent, and the porphycene concentration was about $5 \cdot 10^{-4}$ M. The radicals were shown to be stable over at least several weeks. The anion radicals of H_2PC1 were also generated by potentiostatically controlled electrolysis in THF by using tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte.[7] In this case the porphycene concentration was 10^{-3} M. Optical spectra of the neutral and anion radical porphycenes were measured in a 3-mm flat cell.

The ENDOR and TRIPLE experiments were performed with a self-built computer-controlled X-band spectrometer,[8,9] while for ESR a commerical spectrometer (Bruker ER 200D) was used. The UV–vis spectra of H_2PC1 were recorded with a Cary-219 spectrophotometer.

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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

$$\nu_{\text{ENDOR}}^{\pm} = |\nu_n \pm a_{iso}/2|$$

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.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (FUB, HUJ) and by the Israel Council for Research and Development (HUJ). The Fritz Haber Research Center is supported by the Minerva Gesellschaft für die Forschung GmbH, München, FRG.

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

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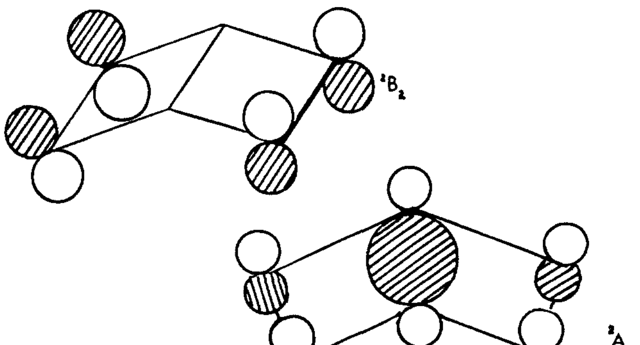
Received July 28, 1988

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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