in line with the experimental results. The preceding analysis is of course somewhat oversimplified for a solid, as the anisotropic parts of the electron–nuclear interactions have not been considered.[21] When these effects are also included, the evidence against a triplet ground state for **1** becomes even stronger and these aspects will be discussed fully in a subsequent paper. In the absence of a contact shift the chemical shift measured here can be compared with those of other diamagnetic trivalent carbon centers. While speculative, the placement of the biradical resonance approximately halfway between the ranges observed for the terminal carbons in allylic anions and cations[19] is consistent with the approximately linear chemial shift variation with charge density exhibited by many series of compounds.[19,20]

In conclusion this work demonstrates that matrix-isolation NMR can be a very powerful tool for following the chemistry of captive intermediates such as **1** in rigid glasses. The spectra reported in this work provide the first direct confirmation that **1** is indeed a singlet ground state, and this will be a useful benchmark in future studies of biradicals with small singlet–triplet gaps. Future work will extend this technique to the direct observation of other captive intermediates such as singlet carbenes and silylenes.

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(21) Chacko, V. P.; Ganapathy, S.; Bryant, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5491-5492.

Dynamics of Bond Conjugation Defects in *trans*-Polyacetylene

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Extensive interest and controversy have been generated by the proposal that the paramagnetic defects observed in *trans*-polyacetylene are topological solitons.[1] Solitons are unique excitations of degenerate 1-D electronic structures and are thought to play a major role in describing the photoexcited states and transport properties of these systems. Polyacetylene, the prototype conducting polymer, is the first material in which these excitations were thought to have been observed. A fundamental aspect of soliton theory as applied to polyacetylene is the high on-chain mobility of the soliton, which presumably transports spin in the pristine material and charge in the doped polymer along the polyene chain[2] at near-phonon frequencies. In this paper, we present ENDOR results on low-spin samples of *trans*-polyacetylene. Our results contradict previous interpretations of ENDOR as well as NMR and EPR experiments that were exclusively based on a model of fast 1-D soliton diffusion.

Soliton theory makes specific predictions about the structure[3] and mobility[3,4] of paramagnetic defects in *trans*-polyacetylene. In principle, the spin density profile of the immobile soliton should be directly observable from the hyperfine couplings obtained by EPR or NMR experiments. At issue for the defect structure is the quantitative form of the spin density profile;[5] that the spin is a π radical and is highly delocalized has been well established.

In practice, the intractable and disordered nature of polyacetylene has limited the observation of hyperfine interactions to the ENDOR spectrum of *cis*/*trans*-polyacetylene composites and to the trans isomer at $T < 4$ K.[6-10] Because *cis*-polyacetylene does not have a degenerate ground-state structure, this result was interpreted as evidence for highly mobile solitons in *trans*-polyacetylene and fixed, immobile solitons in the cis isomer.[10,11] During the thermal treatment that converts the cis isomer to *trans*-polyacetylene, solitons trapped on short segments of the trans isomer are liberated to diffuse freely along the polyene chain, thereby reducing the local hyperfine couplings in *trans*-polyacetylene as observed by ENDOR. This interpretation was supported by NMR proton T_1 and dynamic nuclear polarization (DNP) experiments[12] but was not consistent with ^{13}C NMR T_{1n},[13] NMR nutation,[13] and pulsed EPR experiments.[14]

Samples in which the spin density, morphology, conjugation lengths, and crystallinity are controlled are required in order to characterize unambiguously the magnetic defects in polyacetylene. *cis*-Polyacetylene prepared by the Shirakawa process[15] contains about 1 unpaired spin/30 000 carbon atoms, and the thermal isomerization step that yields the trans isomer consistently increases the spin density by 10 times. Recently, it was shown that *trans*-polyacetylene can be directly prepared giving materials with up to 10 times fewer defects[16,17] than polyacetylene obtained by the Shirakawa process. This material is identical in terms of its IR spectrum, morphology, and crystal structure, but the EPR line width of the magnetic defects was 5 times broader. Since the 10-fold increase in unpaired spin density that accompanies the conversion of *cis*-polyacetylene to the trans isomer greatly complicates the magnetic measurements and their interpretation, we decided to test the soliton model by performing ENDOR experiments on samples of low-spin *trans*-polyacetylene.

Shown in Figure 1A is the spectrum of a sample (95% trans isomer content by IR) which had been prepared as a powder. The spin density of this sample (1 spin/30 000 carbon atoms) is comparable to cis-rich samples prepared by the Shirakawa method. Remarkably, this spectrum shows that the defects in the low-spin *trans*-polyacetylene are identical not with those found in the trans Shirakawa material but rather with those in *cis*-polyacetylene.

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(1) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. Lett.* **1979**, *42*, 1698.

(2) For a review of recent work, see: Skotheim, T. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.

(3) Weinberger, B. R.; Ehrenfreund, E.; Pron, A.; Heeger, A. J.; MacDiarmid, A. G. *J. Chem. Phys.* **1979**, *72*, 4749.

(4) Maki, K. *Phys. Rev. B: Condens. Matter* **1982**, *26*, 2187.

(5) A debate exists over whether the ENDOR spectrum observed for the trapped immobile paramagnetic defect is consistent with the simple soliton model. Thomann et al.[6-8] and more recently Mehring et al.[9] have concluded that the spectrum cannot arise from the spin densities of a simple immobile soliton, while Kuroda et al.[10] concluded that the spectrum is direct evidence for soliton spin densities. This topic has recently been reviewed in great detail elsewhere.[8] Here we simply state that whether the soliton spin density profile corresponds to the ENDOR spectrum is irrelevant to our observations and conclusions presented in this paper.

(6) Thomann, H.; Dalton, L. R.; Tomkiewicz, Y.; Shiren, N. S.; Clarke, T. C. *Phys. Rev. Lett.* **1983**, *50*, 533.

(7) Thomann, H.; Dalton, L. R. *Handbook of Conducting Polymers*; Skotheim, T., Ed.; Marcel Dekker: New York, 1986; Chapter 32.

(8) Thomann, H. *Electronic Magnetic Resonance of the Solid State*; Weil, J., E.; Canadian Chemical Society: Ottowa, Ontario, 1986.

(9) Kahol, P. K.; Mehring, M. *J. Phys. C.* **1986**, *19*, 1045.

(10) Kuroda, S.; Bando, H.; Shirakawa, H. *J. Phys. Soc. Jpn.* **1985**, *54*, 3956.

(11) Heeger, A. J.; Schrieffer, J. R. *Solid State Commun.* **1983**, *48*, 207.

(12) Nechtschein, M.; Devreux, F.; Genoud, F.; Guglielmi, M.; Holczer, K. *J. Phys. Colloq.* **1983**, *44*, 209.

(13) Clarke, T. C.; Scott, J. C. *Handbook of Conducting Polymers*; Skotheim, T. Ed., Marcel Dekker: New York, 1986; Chapter 31.

(14) Shiren, N. S.; Tomkiewicz, Y.; Kazyaka, T. G.; Taranko, A. R.; Thomann, H.; Dalton, L. R.; Clarke, T. C. *Solid State Commun.* **1982**, *44*, 1157.

(15) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.

(16) Baker, G. L.; Shelburne, J. A., III; Bates, F. S. *J. Am. Chem. Soc.* **1986**, *108*, 7377.

(17) The spin density is sample dependent. Typical samples had spin densities ranging from 1 spin/30 000 C atoms to 1 spin/10 000 C atoms.

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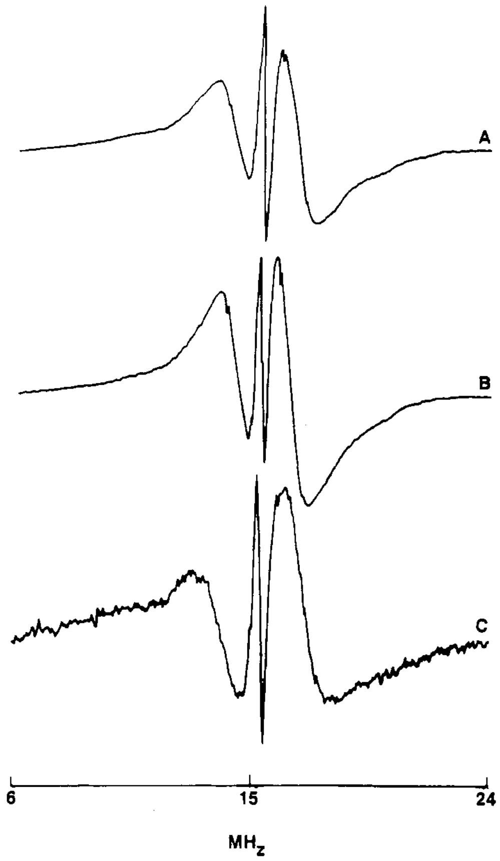

Figure 1. ENDOR spectra obtained for three low spin density *trans*-polyacetylene samples: (A) 95% trans isomer content, powder; (B) 95% trans isomer content, free-standing films; (C) thermally annealed low-spin free-standing film. Experimental conditions were microwave power incident on cavity, 10 mW; radio frequency power, 50 W (nominal); T = 140 K. Narrow spikes are decade markers arising from the radio frequency frequency source. Spectra are composed of two components: local hyperfine and distant ENDOR transitions. The variation in relative intensities between the two components is consistent with the difference in spin densities among the samples. Assignments of hyperfine tensors are the same as previously described.[7,8]

Figure 1B shows that identical results were obtained for low-spin *trans*-polyacetylene prepared as free standing films (also composed of 95% trans isomer).

Within the soliton framework, our results could be interpreted as evidence for fixed spins in these materials, solitons trapped within short trans isomer segments, just as the defects are thought to be trapped in *cis*-polyacetylene. We tested this interpretation by performing an identical thermal treatment on low-spin *trans*-polyacetylene. Any remaining cis isomer segments should be isomerized to the trans isomer, thus permitting the solitons to be freely mobile along the chain. The additional isomerization was confirmed by a slight increase in the trans isomer content as observed by IR and also by a factor of 3 increase in the spin density. Figure 1C shows the ENDOR spectrum for this material. Clearly there is no evidence for mobility of the defects, and the spectrum remains almost identical with that of *cis*-polyacetylene.

We envision two possible mechanisms to explain our results. The loss of local ENDOR structure in *trans*-polyacetylene samples prepared by the Shirakawa method can simply be a result of its high spin density; spin-spin exchange mechanisms represent the major contribution to the apparent dynamic narrowing of hyperfine interactions observed in ENDOR experiments.[9] The alternative explanation is that even after thermal isomerization, all solitons remain trapped in low-spin *trans*-polyacetylene. This would have to occur despite the fact that the polymer is identical structurally, chemically, and spectroscopically with the Shirakawa material. In addition, indistinguishable trapping mechanisms for the Shirakawa material at low temperatures, *cis*-polyacetylene, and low-spin *trans*-polyacetylene are suggested by the similarity of their ENDOR spectra. The absence of any corroborating evidence for additional trapping mechanisms suggests that spin exchange is the correct explanation, contrary to previous interpretations of the ENDOR data.

It is important to note that even though exchange dominates the magnetic properties of polyacetylene, EPR,[3] ESE,[14] NMR,[12] and DNP[18] experiments suggest an additional contribution from a thermally activated dynamic process. Whether slow 1-D motion might be responsible for the activated process is currently under investigation.

Registry No. *trans*-Polyacetylene, 25768-71-2.

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[18] Clark, W. G.; Glover, K.; Mozurkewich, G.; Murayama, C. T.; Sanny, J.; Etemad, S.; Maxfield, M. *J. Physiq. Colloq.* **1983**, *44*, 239.

Wagner-Meerwein Rearrangements of Radical Cations Generated by Triphenylpyrylium Tetrafluoroborate Photosensitized Electron Transfer of Azoalkanes

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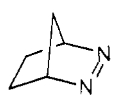
While there has been a surge of activity during the last decade on the chemistry of radical cations,[1] only little information exists on such reactive intermediates derived from azoalkanes. This is particularly surprising in view of the fact that azoalkanes display well-defined photoelectron spectra.[2] Recently, however, the first report[3a] of such species appeared, namely, the radical cation of 1,1′-azoadamantane, generated by chemical oxidation with the thianthrene radical cation. Furthermore, the photochemistry of the reluctant 2,3-diazabicyclo[2.2.2]octene in CCl_4 has been interpreted in terms of the corresponding azoalkane radical cation.[3b] Specifically, excited azoalkane served as donor, transferring an electron to ground-state CCl_4 as electron acceptor. Presently we report that the excited electron acceptor triphenylpyrylium tetrafluoroborate (TPT^+) acquires an electron from ground-state azoalkanes **1-4** as donors, resulting in the respective azoalkane radical cations. Loss of nitrogen from the latter affords rearranged photoproducts (eq 1) which we rationalize to be derived from the intermediary hydrocarbon radical cations.



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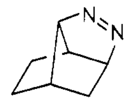

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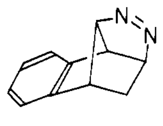

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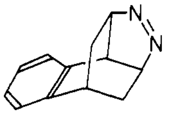

(4)

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[1] (a) Dunkin, I. R.; Andrews, L. *Tetrahedron* **1985**, *41*, 145. (b) Symons, M. C. R. *Chem. Soc. Rev.* **1984**, 393. (c) Todres, Z. V. *Tetrahedron* **1985**, *41*, 2771. (d) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 7210. (e) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155.

[2] (a) Haselbach, E.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Angew. Chem.* **1969**, *81*, 897. (b) Haselbach, E.; Heilbronner, E. *Helv. Chim. Acta* **1970**, *53*, 684. (c) Boyd, R. J.; Bünzli, J. C.; Snyder, J. P.; Heyman, M. L. *J. Am. Chem. Soc.* **1973**, *95*, 6478. (d) Schmidt, H.; Schweig, A.; Trost, B. M.; Neubold, H. B.; Scudder, P. H. *J. Am. Chem. Soc.* **1974**, *96*, 622. (e) Houk, K. N.; Chang, Y.-M.; Engel, P. S. *J. Am. Chem. Soc.* **1975**, *97*, 1824. (f) Gleiter, R.; Schäfer, W. *J. Org. Chem.* **1985**, *50*, 4375.

[3] (a) Bae, D. H.; Engel, P. S.; Hoque, A. K. M. M.; Keys, D. E.; Lee, W.-K.; Shaw, R. W.; Shine, H. J. *J. Am. Chem. Soc.* **1985**, *107*, 2561. (b) Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964.

[4] (a) Ushida, K.; Shida, T.; Walton, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2805. (b) Gassman, P. G.; Hay, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 4227.