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Supplementary Material Available: Analytical data for the compounds whose synthesis is described in the Experimental Section (^{1}H NMR, exact molecular weights, and elemental analyses) and tables of kinetic data for the reaction of 4-MeOArCH(R)Cl (R = CH_2F, CHF_2, CF_3) at increasing concentrations of chloride ion (5 pages). Ordering information is given on any current masthead page.

How Far Can a Carbanion Delocalize? ^{13}C NMR Studies on Soliton Model Compounds[1]

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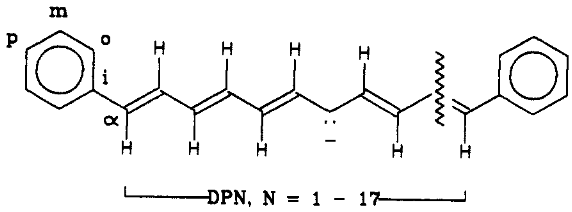
Abstract: For well-defined π systems, ^{13}C chemical shifts are correlated with π-electron density. We have used this correlation to develop models for charge carriers in *n*-doped polyacetylene ("solitons") that allow us to determine if the charge density distribution predicted by the soliton theory is correct. In this investigation, a linear chemical shift/charge density relationship is obtained for anions of the general structure $Ph(CH)_nPh^-$, n = 1, 3, 5, 7, 9, ... (DP*N*), if the average chemical shift (δ_C) of all carbons is plotted against the average charge density (ρ_{av}). Such a plot has allowed us to develop the empirical relationship $\rho_C = (\delta_C - 132.7)/187.3$ and thus to calculate the charge density at each carbon atom. Moreover, comparison with neutral compounds of formula $Ph(CH{=}CH)_nPh$ allows us to define the soliton length, that is, the point at which carbanion delocalization in a linear chain ceases.

Introduction

Although many of the qualitative aspects of charge transport in conductive polymers[2] have their counterparts in classical organic chemistry, the concept of a mobile charge carrier ("soliton") is one of the most difficult to reconcile with the conventional understanding of resonance. According to the soliton theory, the charge carrier in reductively (or oxidatively) doped polyacetylene is a resonance-stabilized carbanion (or carbocation) of finite width with maximum charge at the center of the defect and diminishing amplitude away from the center.[3] Charge transport is thus associated with migration of the charge density wave down the polymer chain (see Figure 1). Such migration will be isoergic only if the solitonic charge density wave has finite width relative to the unsaturation length. Although increased charge density at the center of an odd-alternant hydrocarbon anion has been a familiar aspect of the chemistry of polyenyl anions since the pioneering work of Kloosterziel,[4] less widely understood is the requirement that what would ordinarily be static resonance forms become only dynamically equivalent at long chain length. Figure 1 thus represents the centers of delocalized finite domains as they migrate down the chain. The relevance of the *intra*chain charge-transport mechanism to the overall mechanism of conductivity in bulk polymers, for which *inter*chain charge migration ("intersoliton hopping") is apparently rate limiting, is still the subject of controversy[3e] and is not addressed here.

In order to relate this conclusion from solid-state theoretical physics to the organic chemistry of conductive polymers, we undertook an examination of the effect of increasing chain length on the spectral properties of polyenyl anions, using as our main analytical technique ^{13}C NMR spectroscopy.[1] Use of O'Brien's implementation[5] of the Spiesecke–Schneider relationship,[6] which relates the charge density at individual carbon atoms to the ^{13}C chemical shift, would in principle allow us to determine the charge density at each site of a polyenyl anion of discrete length and extrapolate those charge densities to their limiting values. For reasons of convenience, we chose α,ω-diphenylpolyenyl anions



(DP1, DP3, DP5, ...), asking at what chain length the properties of these anions and *n*-doped polyacetylene converge. In addition to providing precursors that are relatively stable toward polymerization, examination of the chemical shifts as a function of chain length, and comparison with neutral compounds, has allowed us to draw conclusions about the point at which the carbanion ceases delocalization into the aryl ring and thus directly to measure the soliton width. Inasmuch as the use of charge density/chemical shift correlations is still the subject of much controversy, we now report experimental details, analysis of the experimental and

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(1) For a preliminary communication, see: Tolbert, L. M.; Ogle, M. E. *J. Am. Chem. Soc.* **1989**, *111*, 5958.

(2) A number of excellent monographs on the subject of conducting polymers are now available: (a) Skotheim, T. J., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vols. 1 and 2. (b) Chien, J. C. W. *Polyacetylene: Chemistry, Physics, and Materials Science*; Academic Press: New York, 1984. (c) Seanor, D. A., Ed. *Electrical Properties of Polymers*; Academic Press: New York, 1982. (d) For an excellent "layman's guide", see: Kaner, R. B.; MacDiarmid, A. G. *Scientific American* **1988**, February, 106–111.

(3) (a) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. Lett.* **1979**, *42*, 1698. (b) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev.. Sect. B.* **1980**, *22*, 2099. (c) Su, W. P. In *Handbook of Conducting Polymers*; Skotheim, T. J., Ed.; Marcel Dekker: New York, 1986; pp 757–794. (d) Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W.-P. *Rev. Mod. Phys.* **1988**, *60*, 781. (e) Roth, S. *Mater. Sci. Forum* **1989**, *42*, 1.

(4) (a) Kloosterziel, H.; Werner, M. A. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 124. (b) Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 215. (c) Bates, R. B.; Gosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* **1967**, 205.

(5) O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410.

(6) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468.

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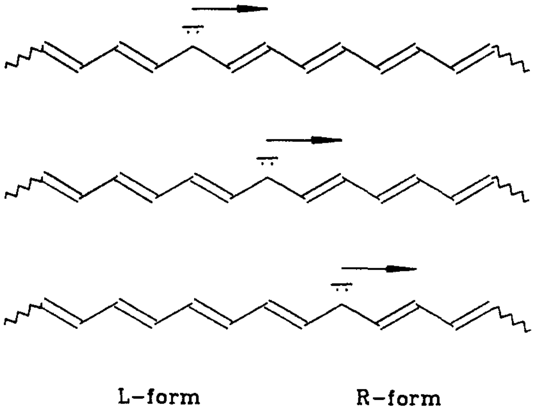

Figure 1. Coupled soliton modes in *n*-doped polyacetylene.

theoretical underpinnings for such correlations, and further observations of the curious properties that result in the region between discrete polyenes and "infinite" polyacetylene.

Background

Charge Density vs ^{13}C Chemical Shift. That a relationship exists between chemical shift and charge density has been axiomatic in organic chemistry since the early days of NMR. The first-order approximation is given by eq 1.[7] Although proton spectra are

$$\delta_C = \alpha\rho + \delta_O \qquad (1)$$

heavily dependent upon anisotropic effects such as ring currents, carbon spectra are relatively insensitive to such effects and have yielded to various empirical treatments. Since charge density is a somewhat theoretical construct, Spiesecke and Schneider (SS) and, later, Olah[8] used a series of aromatic ions for which charge densities at individual carbons are equivalent by means of symmetry and arbitrarily assigned the total charge to the carbon atoms. Assuming that the proportionality constants in eq 1 are independent of carbon atom for sp^2-hybridized systems, O'Brien extracted the proportionality constants α and δ_O from the average chemical shifts and average charge densities of a series of charged and uncharged species and thus was able to use a more extensive set of experimental spectra. The fitting parameters obtained are similar to the SS parameters. Linear least-squares treatment provided the "best fit" equation $\delta_C = 156.3\rho + 133.2$. Finally, the most extensive example of this empirical approach is that of Hunadi,[9] who drew some rather sweeping conclusions about the degree of aromaticity in several classes of homoaromatic and methano-bridged hydrocarbon ions by examining the magnitude of the slope α as a function of structure. Irrespective of the validity of Hunadi's treatment, which we dispute in the following text, our error analysis of these data leads us to conclude that the fitting parameters he obtained are indistinguishable from those of SS, Olah, and O'Brien. Figure 2 contains the data from five studies, including a number of aromatic and acyclic unsaturated ions, and indicates relatively good statistical fits to the formula $\delta = 156.2 \pm 2.6\rho + 131.9 \pm 0.4$ with a correlation constant of 0.991. Thus, the slopes of ^{13}C chemical shift/charge density correlations per se must be regarded as unreliable guides to aromaticity. Such correlations may provide useful qualitative guides to charge density distributions in resonance-stabilized carbanions and, in carefully defined cases, may provide quantitative data as well. Inasmuch as our analysis of charge distribution in linear carbanions related to *n*-type solitons depends upon such relationships, it behooves us to examine the origin of this correlation to determine its validity for our application.

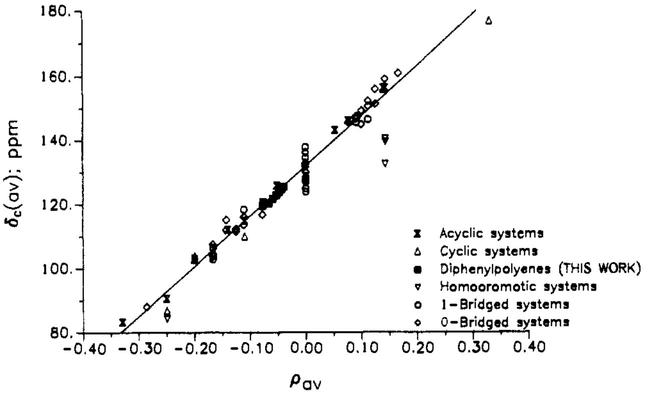

Figure 2. Comparison of data obtained by Hunadi, Olah, Spiesecke–Schneider, and this work.

Origin of the Charge/Chemical Shift Effect. The main contribution to ^{13}C chemical shift anisotropy is dominated by the paramagnetic term σ_b (see eq 2).[10] This term arises from the coupling of the magnetic field with the orbital angular momentum through the operator M_j in the associated Ramsey equation (eq 3).

$$\sigma^a = \sigma_a{}^{AA} + \sum_{A \neq B} \sigma^{AB} + \sigma^{A,\mathrm{ring}} \qquad (2)$$

$$\sigma_{\mathrm{p}} = -\frac{e^2\hbar^2}{m^2c^2}\sum_l\sum_m \frac{\langle\phi_l|\sum_j M_f/r_j^3|\phi_m\rangle\langle\phi_m|\sum_j M_j|\phi_l\rangle + CC}{E_m - E_l} \qquad (3)$$

Pople derived a simplified version of the Ramsey equation based upon an LCAO approach that permits an approximate solution using the coefficients of the 2p atomic orbitals in the LCAO eigenfunctions in which the term $\langle r_0{}^3\rangle$ is a screening term dependent upon both the atomic number and the atomic charge (see eq 4).[11,12] The significance of the Pople equation is that it has

$$\sigma_{\mathrm{p}x} = -\frac{e^2\hbar^2}{m^2c^2}\langle r^{-3}\rangle \sum_i^{\mathrm{occ}} \sum_k^{\mathrm{unocc}} \frac{(c_{iyA}c_{kzA} - c_{izA}c_{kyA})\sum_B(c_{iyB}c_{kzB} - c_{izB}c_{kyB})}{E_k - E_i} \qquad (4)$$

nonzero terms only for interactions between occupied and unoccupied molecular orbitals consisting of orthogonal 2p atomic orbitals, since the effect of the orbital angular momentum operator M_j is to couple filled and unfilled orthogonal orbitals perpendicular to the magnetic field. *The practical result is that π–π*-type (HOMO–LUMO) interactions in planar unsaturated systems make no contribution to parametric shifts*, which, instead, are dominated by σ–π^* and π–σ^* interactions.[10c]

If we use the neglect of overlap approximation on the LCAO's, we can discard all products between coefficients on nonadjacent atoms and reduce eq 4 to eq 5. Fraenkel has discussed use of

$$\sigma_{\mathrm{p}x} = -\frac{e^2\hbar^2}{m^2c^2}\langle r^{-3}\rangle_{2\mathrm{p}} \sum_i^{\mathrm{occ}} \sum_k^{\mathrm{unocc}} \frac{(c_{iyA}^2 c_{kzA}^2 - c_{izA}^2 c_{kyA}^2)}{E_k - E_i} \qquad (5)$$

the "average energy approximation" in which the average energy between the σ and π^* or π and σ^* orbitals (ca. 10 eV) replaces

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[7] Although most treatments relate chemical shift to *π-electron* density, it is experimentally valid, and improves the statistics, to speak of *π-charge* density, for which the intercept δ_O corresponds to the "best fit" chemical shift of a neutral olefin rather than the chemical shift of a hypothetical carbon atom of charge +1. Therefore, the values reported here from the literature will be transformed to conform to eq 1.

[8] Olah, G. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1430.

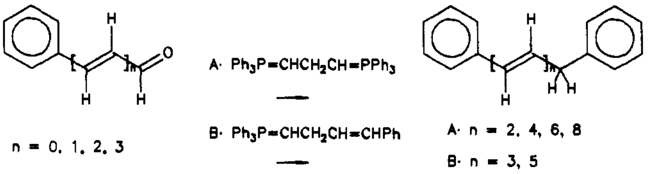
[9] (a) Hunadi, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6889. (b) Irrespective of the validity of Hunadi's conclusions, we believe there are not enough points in his treatment of homoaromatic systems to draw statistically meaningful conclusions.

[10] For extended treatments of chemical shift anisotropy and charge density, see: (a) Tokuhiro, T.; Fraenkel, G. *J. Am. Chem. Soc.* **1969**, *91*, 5005. (b) Gutzner, J. B. In. *Recent Advances in Organic NMR Spectroscopy*; Lambert, J. B., Rittner, R., Eds.; Norell Press: Landisville, NJ, 1987; pp 17–42. (c) Strub, H.; Beeler, A. J.; Grant, D. M.; Michl, J.; Cutts, P. W.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 3333. This paper provides an excellent demonstration that the chemical shift tensors in the plane of aromatic rings, which incorporate σ-π interactions, are large and linear with charge, while the chemical shift tensor perpendicular to the plane, which incorporates σ-σ interactions only, is small and nonlinear.

[11] Pople, J. A. *J. Chem. Phys.* **1962**, *37*, 53.

[12] For simplicity, only the *x* component of the paramagnetic shielding tensor is represented.

Scheme I. Synthetic Scheme for Diphenylpolyenes



the "energy gap" term of eq 5.[10a] This approximation fails for hydrocarbon anions possessing nonbonding electrons in σ-type orbitals, which by definition have small σ–π^* transitions. For example, C-1 of phenyllithium has a chemical shift of 188 ppm, 40 ppm downfield from benzene![13] It also fails for ions that have considerable deviations from nonplanarity, e.g., homoaromatic ions. Conclusions drawn from magnitudes of the charge density/chemical shift correlation for such systems must be viewed with strong skepticism.[9b] Moreover, as Fraenkel has pointed out,[10a] use of the average energy approximation results accounts for roughly half the 160 ppm/electron chemical shift anisotropy. Inclusion of additional excitation energies yields the remaining contributions to the linear dependence. For resonance-stabilized carbanions (or carbenium ions) in which the nonbonding electrons are in the π system, the σ–π energy gap will be large and the average energy approximation qualitatively valid. Using this approximation, we finally derive eq 6. If we assume that the σ

$$\sigma_{px} = -\frac{e^2\hbar^2}{m^2c^2}\langle r^{-3}\rangle_{2p}\langle \mathrm{E}\rangle\sum_{i}^{\mathrm{occ}}\left(c_{iyA}{}^2\sum_{k}^{\mathrm{unocc}} c_{kzA}{}^2 - c_{izA}{}^2\sum_{k}^{\mathrm{unocc}} c_{kyA}{}^2\right) \qquad (6)$$

orbitals, which represent the carbon–hydrogen framework, are highly localized, the non-π-system coefficients in eq 6 will be independent of charge or structure. Thus, the charge-dependent terms in eq 6 are in the sums of the squares of coefficients over occupied orbitals as well as unoccupied orbitals in the π system, although for carbanions the π–σ^* interactions should be the major contributors. Moreover, if we recognize that, for normalized LCAO's, $\sum_{\mathrm{unocc}}c^2 = 1 - \sum_{\mathrm{occ}}c^2$, we see that both terms in eq 6 contain contributions due to sums of squares of occupied atomic orbitals, i.e., the chemical shift anisotropy depends linearly on π charge.

These arguments notwithstanding, there remains considerable controversy over the use of charge density/chemical shift correlations. In cases where large deviations from the 160 ppm/electron relationship are observed, these are generally related to paramagnetic ring current effects.[14] Moreover, assignment of charge is, in a theoretical sense, somewhat arbitrary. If we make this arbitrary assignment of all the net charge to the valence carbon orbitals, recognizing that this assignment will be only qualitatively correct, there is a self-consistency built into the calculation that allows for considerable cancellation of error.

Results

Synthesis of α,ω-Diphenylpolyenes. 1,5-Diphenylpentadiene (DP5-H), 1,9-diphenylnonatetraene (DP9-H), 1,13-diphenyltridecahexaene (DP13-H), and 1,17-diphenylheptadecaoctaene (DP17-H) were prepared by addition of the appropriate aldehyde to the bis(ylide) of trimethylenebis(triphenylphosphonium) bromide. 1,7-Diphenylheptatriene (DP7-H) and 1,11-diphenylundecapentaene (DP11-H) were prepared by alkylation of triphenylphosphonium methylide with 3-bromo-1-phenyl-1-propene followed by addition of cinnamaldehyde and 7-phenylhepta-2,4,6-trienal, respectively. In each case, the basic conditions of the reaction led to significant double-bond isomerization, producing as the major product the terminal benzyl isomer shown in Scheme I. 1,3-Diphenylpropene (DP3-H) was prepared via the Bamford–Stevens reaction on the tosylhydrazone of 1,3-diphenyl-2-propanone. Diphenylmethane (DP1-H), *trans*-stilbene (DP2), *trans,trans*-1,4-diphenyl-1,3-butadiene (DP4), *trans,trans,trans*-1,6-diphenyl-1,3,5-hexatriene (DP6), and 1,8-diphenyl-1,3,5,7-octatetraene (DP8) were commercially available.

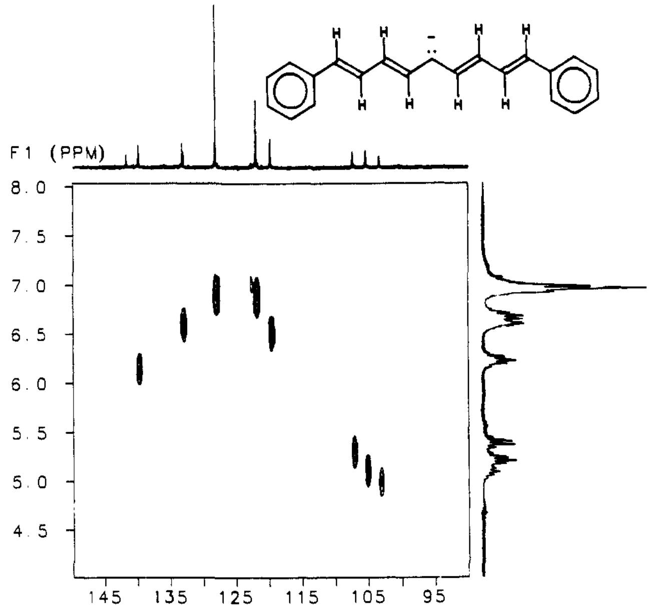


Figure 3. HETCOR spectrum of DP9.

Generation of Anions. Treatment of the appropriate hydrocarbon precursors DP*N*-H in Me$_2$SO solution with potassium (methylsulfinyl)methide ("dimsyl") produced immediate color formation that varied from orange to deep blue-black to colorless as the chain length increased. The higher homologues were poorly soluble and required filtration under inert atmosphere to obtain homogeneous solutions for NMR analysis. In the case of DP17 and higher homologues, anisotropic line broadening prevented acquisition of analyzable spectra. However, anions DP1–DP13 yielded quite satisfactory ^{13}C and ^{1}H spectra for further analysis. Curiously, although DP3 exhibited both *E,E* and *E,Z* conformers in accordance with literature studies in non-ion-pairing solvents,[15] the higher homologues showed little conformational diversity apart from absorbances of $<\sim$5% intensity that apparently corresponded to *Z* conformers. By analogy with DP3, for which proton and carbon chemical shifts had similar frequency separation and, therefore, similar exchange kinetics, such conformers in the higher homologues should have been visible in the carbon spectra. We conclude that the carbon chemical shifts corresponded to the single isomer represented in the proton spectra. Moreover, the coupling constants, which ranged from 11.7 Hz for central protons to 14.8 Hz for the α protons, are consistent only with the all-trans, planar conformation in which increased bond localization at the ends of the chain leads to higher coupling constants.[4c] The ^{13}C chemical shifts of the anions were found to be devoid of counterion effects as indicated by employing as base CH$_3$SOCH$_2^-$K$^+$/18-crown-6 in Me$_2$SO-d_6. The ^{13}C chemical shift of C-1 of DP1 was obtained only after addition of Me$_2$SO-h_6 to the deprotonated substrate, since facile protium/deuterium exchange otherwise led to line broadening and an isotope effect on the chemical shift. Similarly, DP3 underwent slow exchange with Me$_2$SO-d_6 to yield deuteriated anion, which exhibited an isotope effect on the C-1 chemical shift. Although assignment of ^{13}C chemical shifts for anions DP1–DP7 was straightforward with use of two-dimensional (HETCOR)

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(13) Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1984**, *106*, 4627.

(14) (a) Eliasson, B.; Edlund, U.; Müllen, K. *J. Chem. Soc., Perkin Trans. 2* **1986**, 937. (b) Müllen, K. *Chem. Rev.* **1984**, *84*, 603.

(15) For previous work on ^{1}H and ^{13}C NMR studies of DP3, see: (a) Burley, J. W.; Ife, R.; Young, R. N. *J. Chem. Soc., Chem. Commun.* **1970**, 1256. (b) Burley, J. W.; Young, R. N. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1006, 1843. (c) Bushby, R. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1419. (d) Boche, G.; Schneider, D. R. *Tetrahedron Lett.* **1976**, 3657. (e) Freedman, H. H.; Sandel, V. R.; Thill, B. P. *J. Am. Chem. Soc.* **1967**, *89*, 1762. (f) Boche, G.; Buckl, K.; Martens, D.; Schneider, D. R. *Liebigs Ann. Chem.* **1980**, 1135. (g) Bushby, R. J.; Ferber, G. J. *Tetrahedron Lett.* **1974**, 3701. (h) Bushby, R. J.; Ferber, G. J. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1688. (i) Heiszwolf, G. J.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1345. (j) Burley, J. W.; Young, R. N. *J. Chem. Soc. C* **1971**, 3780.

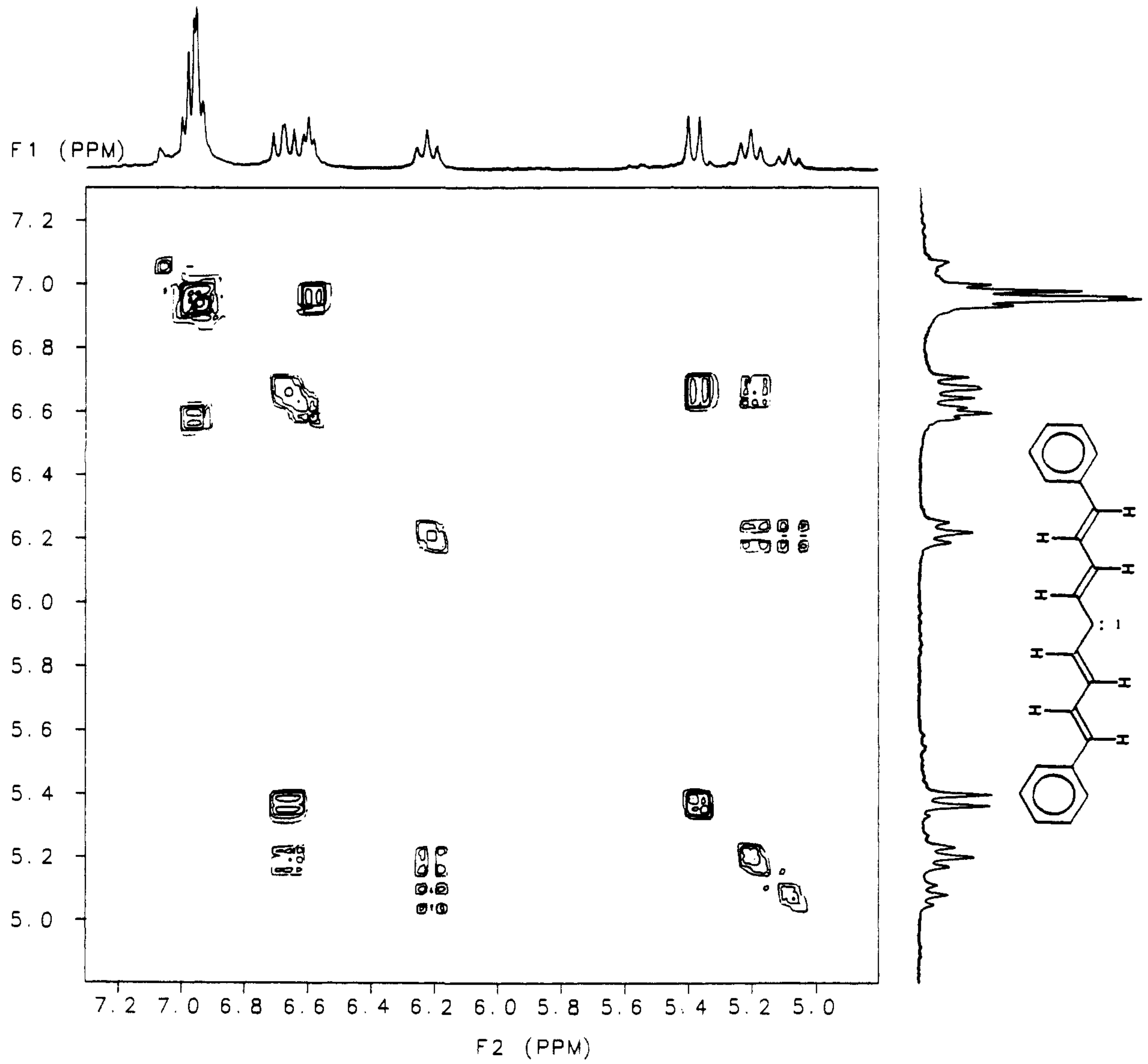

Figure 4. COSY spectrum of DP9.

spectroscopy (Figure 3), the higher homologues required more rigorous examination. In particular, DP9 presented ambiguities associated with the proton assignments from which the ^{13}C assignments were derived. Thus, it was necessary to use the COSY method to assign the proton absorptions first. Homonuclear 2D (COSY) NMR spectroscopy allowed unambiguous assignment of proton chemical shifts in all cases. Figure 4 shows DP9 as a representative example of ^{1}H chemical shifts that were readily assigned from the doublet at δ 5.38 (J = 14.4 Hz) corresponding to the C-1 proton. Heteronuclear (HETCOR) $^{13}C-^{1}H$ spectroscopy allowed indirect assignment of the ^{13}C chemical shifts. The HETCOR of DP9 with carbon and proton assignments is shown in Figure 3. The assignment of all chemical shifts for anions DP1–DP13 is presented in Table I of ref 1. In all cases, the nuclei corresponding to the odd-numbered carbon atoms had upfield chemical shifts (excess charge densities) vs the even-numbered counterparts. More illustrative of this is the plot of the ^{13}C spectra of the linear odd-alternant α,ω-diphenylpolyenyl anions (Ph-$(CH)_n$Ph$^-$, n = 1, 3, 5, 7, 9, 11, 13) relative to one another as shown in Figure 5.

ESR Spectroscopy. The failure of DP17 to yield useable NMR spectra suggested the participation of paramagnetic line broadening for the longer anions. In order to test this possibility, ESR spectra of anions DP5–DP17 were prepared by deprotonation of the hydrocarbons with *n*-butyllithium or potassium *tert*-butoxide in tetrahydrofuran. In the case of DP9–DP17, strong ESR signals with an apparent g factor of 2.0033 for DP17, corresponding to formation of carbon-centered radicals, were obtained (see Figure 6). No attempt was made to quantify the concentration of paramagnetic species.

Discussion

Calculation of Charge Densities. With the availability of the unambiguously assigned ^{13}C chemical shifts in hand, we proceeded to apply the O'Brien treatment. Excellent linear least-squares statistics were obtained from a plot of average charge density ($-1/N$) vs average chemical shift to yield the empirical relationship represented by eq 1, with α = 187.3 and δ_O = 132.7, after neglecting the first member of the series DP1, which falls off the Spiesecke–Schneider correlation line (Figure 7 is plotted vs $1/N$ for the ensuing discussion). Although the large charge density on C-1 might cause substantial chemical shift anisotropy due to ion pairing, the absence of significant chemical shift differences for DP1 and DP3 in the presence of 18-crown-6 indicates that ion pairing is not a factor. Rather, significant geometry changes are known to occur in DP1, resulting in a central bond angle of 132°.[16] This again reemphasizes the importance of restricting the O'Brien treatment to planar, sp^2-hybridized hydrocarbons.

Even restricting our attention to the limited subset DP5 to DP13, is this average charge density/chemical shift correlation valid? Two facts arouse doubt. First, the value α of 187.3 ppm/electron is considerably larger than that calculated for other

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[16] (a) Crystal structure: Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 2174. (b) Calculation: Adams, S. M.; Bank, S. *J. Comput. Chem.* **1983**, *4*, 470.

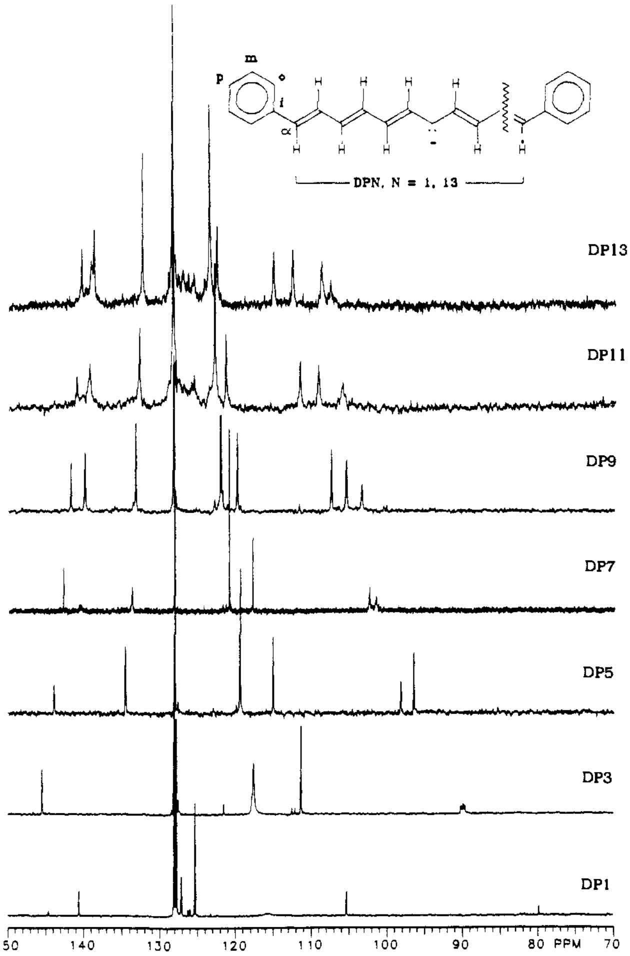

Figure 5. Stacked spectra of diphenylpolyenyl anions.

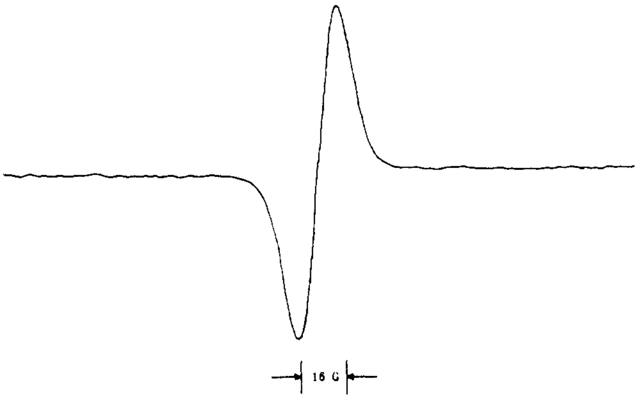

Figure 6. ESR spectrum of DP17.

systems, which cluster around 160 ppm/electron (see Figure 2). In fact, differences in α from 160 ppm/electron have been cited, with some controversy, to answer questions about aromaticity and antiaromaticity.[17] Second, the diminishing HOMO–LUMO gap with chain length, which necessarily results in a diminished σ–π^* or σ^*–π energy term in eq 5,[18] could lead to a larger chemical shift anisotropy than would be explained merely by charge density effects. Again, such a result has been cited for antiaromatic species, which have low HOMO–LUMO gaps by definition.[19] To

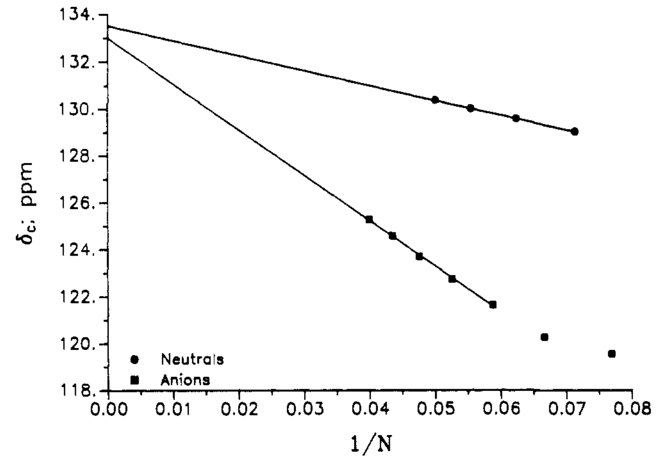

Figure 7. Average ^{13}C vs $1/N$ for neutral and anionic diphenylpolyenes.

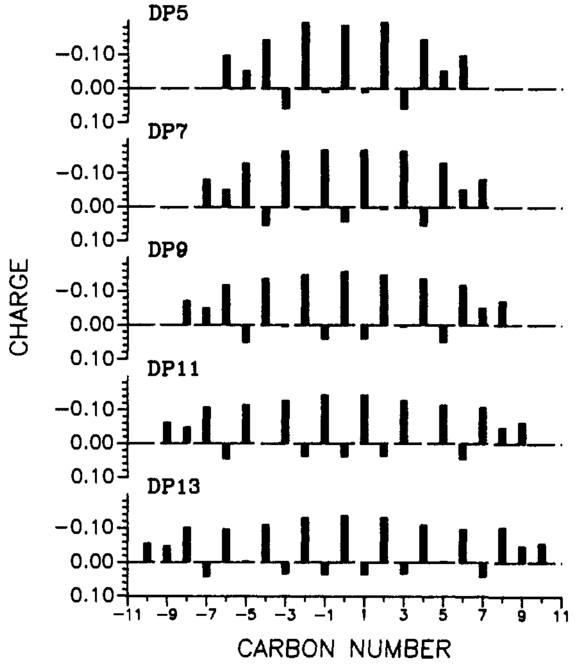

Figure 8. Histogram plot of DPN charge densities.

obtain a partial answer to this question, we appeal to the neutral, even-alternant diphenylpolyenes stilbene (DP2), 1,4-diphenyl-1,3-butadiene (DP4), 1,6-diphenyl-1,3,5-hexatriene (DP6), and 1,8-diphenyl-1,3,5,7-octatetraene (DP8). The HOMO–LUMO gaps for these systems have been shown to correlate with $1/N$, where N is approximately the chain length including the phenyl groups.[20] The average carbon resonance, then, should show downfield chemical shifts as the chain length increases. For the sake of comparison, the data for the neutral polyenes are plotted in Figure 7 along with those for the anions. As can be seen, a diminishing HOMO–LUMO gap[21] is correlated with downfield average chemical shift.[18] This effect is misleading, however, since the chemical shifts of individual atoms are invariant with respect to chain length (see the following text). Of course, energy gap effects, if any, are going to be much more significant for the anions, which have longer wavelength absorptions. Irrespective of energy gap, however, anionic diphenylpolyenes exhibit a similar limiting chemical shift value to the neutrals at infinite ($1/N = 0$) chain lengths. As Eliasson, Edlund, and Müllen (EEM) have suggested,[14] we can correct for local anisotropy effects by appealing to the neutral polyene data. That is, the value of α = 187.3

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(17) Bausch, J. W.; Gregory, P. X.; Olah, G. A.; Prakash, G. K. S.; Schleyer, P. v. R.; Segal, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 3633.

(18) For odd-alternant hydrocarbons at the Hückel level, both n and σ levels remain constant. Thus, both π-π^* and σ-π^* differences should have the same correlation.

(19) (a) Edlund, U.; Eliasson, B. *J. Chem. Soc., Chem. Commun.* **1982**, 950. (b) Becker, B. C.; Huber, W.; Schnieders, C.; Müllen, K. *Chem. Ber.* **1983**, *116*, 1573. (c) Schnieders, C.; Müllen, K.; Huber, W. *Tetrahedron* **1984**, *40*, 1701.

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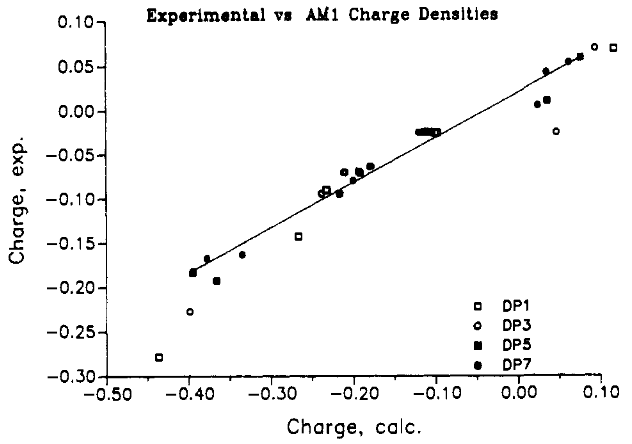

Figure 9. Experimental vs calculated (AM1) charge densities for DP1–DP7.

ppm/electron could be corrected by the slope contribution from neutral polyenes (62.8) to yield a "corrected" α of 124.5.

Using the parameters obtained by the O'Brien treatment, we have calculated the charge density distribution in each member of the series DP*N* (see Table I of ref 1 and Figure 8). We note that use of the EEM approach would yield nearly the same charge densities from the corrected chemical shifts through cancellation of the α term. As can be seen from Figure 8, the charge density localizes at the center of the polyenyl anion, with a decreasing proportion of charge localized on the ends as the chain length increases.[1]

An important and controversial question is whether parameters derived from *average* charge densities, which presumably involve considerable cancellation of error, can be applied to *individual* charge densities. In order to provide insight to this question, we carried out AM1 calculations on DP1–DP7.[22] A plot of experimentally determined vs calculated charge densities is shown in Figure 9. For DP5 and DP7, linear regression yields excellent statistics (intercept = 0.019, slope = 0.51, ρ = 0.984). Both DP1 and DP3 show substantial deviations, consistent with the deviation from the O'Brien plot and with geometric distortions noted previously.[16]

Figure 9 further illuminates the difficulties involved in charge density determinations. Such calculations are based upon Mulliken populations, which may not be quantitatively meaningful, particularly at the semiempirical level, and which may exaggerate charge density on carbon.[23] A number of other approaches have addressed the assignment of charge based upon topological considerations.[24] Thus, we conclude that, at least for the linear anions, energy gap effects are not overwhelming and our calculation of the charge density distribution remains qualitatively valid. Whether it is quantitatively valid awaits a higher level of calculation.

What Is the Soliton Width? To say that charge localizes at the center of polyenyl anion is not necessarily to define the width of the soliton. In fact, all calculations on soliton charge densities include diminishing but nonzero values far removed from the center, and it is conventional to speak of the "full width at half-height". However, there are practical limits to this delocalization, and we wondered if we could use NMR spectroscopy to determine this delocalization width. Fortunately, a comparison of even-alternant neutrals and odd-alternant anions allowed us to make this determination.[25] The question is posed as follows:

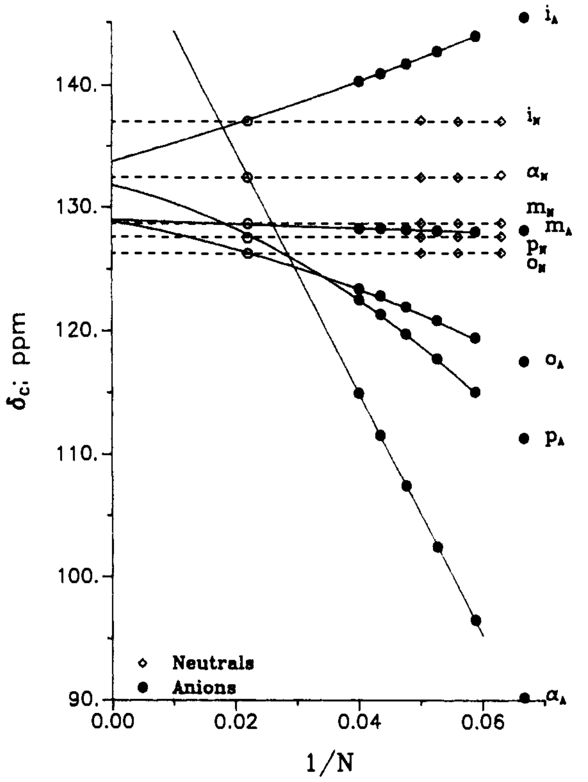

Figure 10. Convergence of anionic and neutral polyene chemical shifts.

Given neutral and anionic diphenylpolyenes of length *N*, at what point do the magnetic properties of the neutrals and anions converge? That point will give us the soliton width. Such a determination depends upon an extrapolation of what may be asymptotic behavior, and we present both a first- and a second-order approach.

Curiously, a plot of chemical shift vs 1/*N*, where *N* is the *total* carbon number, is nearly linear for ortho, meta, para, ipso, and α carbon atoms for all anions higher than DP1 and constant for all neutrals higher than DP2. This result is reminiscent of, and related to, the energy gap correlation.[20] The two sets of *aromatic* chemical shifts converge at a point that may be obtained by inspection, although linear-regression analysis of the data allows us to calculate the crossing point by least-squares treatment, using the formula:

$$N = \frac{\sum_i \alpha_i^2}{\sum_i (\delta_{O_i} - \delta_{C_i})\alpha_i} \qquad (7)$$

In this case, α_i represents the slope of the linear regression line for each atom *i*, δ_{C_i} the limiting chemical shift for each atom *i*, and δ_{O_i} the corresponding chemical shifts for the neutral atoms. Application of eq 7 yields the value $N = 38$, which after correction for the presence of two phenyl groups yields a soliton width of 26.[25] A second-order polynomial fit to the data (see Figure 10) yields a slightly different convergence point, $N = 45$, which now includes the α carbons. After correction for the two phenyl groups and two α carbons, the extrapolated soliton width is 31. Within the limits of these two extrapolations, a soliton full width of approximately 30 is gratifyingly close to that predicted by theory and, significantly, does not depend upon a calculation of charge densities!

Soliton Width and Soliton Mobility. Figure 10 poses a perplexing question. That is, what is the significance of the extrapolation in the region beyond the limiting soliton width of 31? Our results demonstrate that at that limiting soliton width the phenyl groups cease delocalization of the negative charge. Further increases in the polyene length necessarily provide no further stabilization, and structures that locate the center of the soliton at different carbon atoms beyond C-15 are of identical energy.

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(22) AM1 was accessed through AMPAC, available from Quantum Chemistry Program Exchange, Program No. 506, and is not dimensioned for molecules as large as DP9.

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Thus, the structures in Figure 1 are coupled through phonon modes and the soliton is mobile.

Finally, we note that the bulk conductivity of doped polyacetylene is limited by contact resistance associated with charge transfer between chains ("intersoliton hopping") rather than charge transport within a single chain, since the conjugation length even in the most favorable case for high molecular weight polyacetylene at best corresponds to micrometers. Within individual unsaturated polymer chains, however, we can now conclude that charge transport along the polymer chain may occur through an activated process involving mobile charged solitons. Such a conduction mechanism would be operative at the nanostructure level, that is, for devices in which conductivity is that of individual chains or ensembles and for which interchain hopping is not required.

Experimental Section

Materials. All manipulations using anions were carried out in an atmosphere of argon that had been deoxygenated with a BASF catalyst. Tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl under argon prior to use. Dimethyl sulfoxide (Me_2SO, h_6 and d_6) was dried and distilled under argon from calcium hydride and deoxygenated according to the procedure of Bordwell.[26] Solutions of dimsylpotassium were obtained from the reaction of Me_2SO with potassium hydride and were titrated with potassium hydrogen phthalate (KHP) prior to use. 18-Crown-6 was dried under reduced pressure (0.2 Torr) for 48 h. Diphenylmethane was obtained commercially, and the other substrates were prepared by directed synthesis (see the following text). Reported yields were not optimized. Liquids were usually fractionally distilled under reduced pressure, and further purification was effected by chromatography on alumina with hexane as eluent. Solids were purified by multiple recrystallizations and dried at ~1 Torr pressure for 24 h. Melting points were determined on an Electrothermal capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet 520 FT-IR spectrometer. ^1H NMR (Varian Gemini 300), gas chromatography (Hewlett-Packard 5890), and mass spectrometry (VG Instruments 70SE) were also used to determine the purity of the substrates, which were stored in the dark under argon at −30 °C. All glassware was dried at 125 °C overnight and flushed with argon immediately prior to use. All transfers were conducted via cannula or gas-tight syringe. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Anions and NMR and ESR Measurements. Anions for the NMR measurements were generated at room temperature directly in NMR tubes equipped with rubber septa that were evacuated and purged with deoxygenated argon prior to sample introduction unless indicated otherwise. Sparingly soluble anions (DP11 and DP13) were filtered through Millipore Millex-LS 5.0-μm filters attached to a gas-tight syringe. In the cases of DP*N*, *N* = 1, 3, 5, 7, 9, studies were conducted employing 18-crown-6 as a complexing agent for potassium cation as well as for neat samples. Spectra were recorded on the Varian Instruments XL-400 (^1H, 399.9, MHz; ^{13}C, 100.6 MHz) spectrometer.[27] All NMR spectra were recorded at ambient temperature in Me_2SO-d_6 or $CDCl_3$ and reported in parts per million with the solvent peak as reference.

Anions for ESR measurements were prepared similarly, with tetrahydrofuran as solvent and either butyllithium or potassium *tert*-butoxide as base. ESR spectra were recorded on a Varian E-Line Century Series spectrometer with 2,2-diphenyl-1-picrylhydrazyl (DPPH) as reference.

Diphenylmethane (DP1-H). Diphenylmethane was obtained commercially and was distilled prior to use.

1,3-Diphenylpropene (DP3-H). In a modification of the procedure reported by Bamford and Stevens,[28] 1,3-diphenyl-2-propanone tosylhydrazone[29] (5.68 g, 15.0 mmol) in 60 mL of tetrahydrofuran was stirred under argon atomsphere at 0 °C for ca. 15 min. To this solution was added *n*-butyllithium (18.8 mL of a 2.4 M solution in hexane, 45.1 mmol), which produced a deep blue-red color. Nitrogen evolution was monitored with a bubbler. The reaction was allowed to warm to room temperature after 1 h and stirred an additional 15 h. After being quenched at 0 °C with dilute hydrochloric acid, the resulting precipitate was filtered. The filtrate was extracted with ether, dried over Na_2SO_4, and concentrated under reduced pressure to produce a yellow oil. Distillation of the crude product (101 °C (0.5 Torr)) produced the 1,3-diphenylpropene (2.69 g, 92.3%, primarily trans) as a colorless oil. Chromatography on alumina with hexane as eluant afforded analytically pure product in a 19:1 trans to cis ratio. The spectral data corresponded to the literature values.[30]

1,5-Diphenylpentadiene (DP5-H). A mixture of isomers was prepared by a modification of Wittig's procedure.[31] To a suspension of trimethylenebis(triphenylphosphonium) bromide[32] (14.5 g, 20.0 mmol) in tetrahydrofuran (ca. 120 mL) maintained at −78 °C was added 42.1 mmol of *n*-butyllithium (18.3 mL of a 2.3 M solution in hexane) dropwise. The orange mixture was allowed to stir for 3 h at −78 °C, after which time it was allowed to warm to room temperature (1 h) and a deep red solution was observed. The reaction was again cooled to −78 °C, freshly distilled benzaldehyde (4.25 g, 40.0 mmol) in tetrahydrofuran (20 mL) was added, and the reaction was heated at reflux for 12 h and then quenched at 0 °C with distilled water (15 mL). The triphenylphosphine oxide was removed by filtration, and after extraction with ether (3 × 100 mL) and drying over $MgSO_4$, concentration in vacuo afforded the crude compound (mixture of isomers) as a light green oil. Distillation (145–150 °C (0.25 Torr)) followed by chromatography on alumina with hexane as eluant afforded 2.47 g (56.1%) of the compound as a colorless liquid (lit.[33] mp 33–35 °C). IR (neat): 3024.4–3100.8, 2854.4–2953.4, 1597.5, 1494.0, 1451.9, 1428.9, 1072.8, 1028.8, 988.4, 948.8, 916.0, 769.4, 744.4, 698.0 cm^{-1}. ^1H NMR (Me_2SO-d_6, 300 MHz (major isomer): δ 3.44 (d, 2 H, *J* = 7.1 Hz), 5.99 (dt, 1 H, *J* = 15.3 Hz, 7.2 Hz), 6.26 (m, 1 H), 6.51 (d, 1 H, *J* = 15.8 Hz), 6.89 (dd, 1 H, *J* = 15.8, 10.4 Hz), 7.20–7.44 (m, 10 H, ArH).[34] MS *m/e* (intensity): 220 (42.5, M^+), 178 (13.5), 143 (14.3), 129 (100.0), 115 (28.7), 103 (7.1), 91 (36.1). NMR simulation demonstrated that the major isomer was the trans,trans isomer of 1,5-diphenyl-1,3-pentadiene. GC/MS indicated the presence of all seven possible isomers.

1,9-Diphenylnona-1,3,5,7-tetraene (DP9-H).[35] 1,9-Diphenylnona-1,3,5,7-tetraene was prepared in an analogous fashion to 1,5-diphenylpentadiene from trimethylenebis(triphenylphosphonium) bromide (14.5 g, 20.0 mmol) and cinnamaldehyde (5.28 g, 40.0 mmol). The workup procedure produced the crude product as a dark oil. Purification was achieved by either of two ways: (1) Chromatography of the crude material on silica gel with chloroform as eluant and isolation of the yellow band followed by recrystallization in boiling ethanol (EtOH) afforded the product as a light yellow, fluffy solid with mp 113–114 °C. (2) Ethanol was added to the black oily residue from the workup and the crude product was allowed to solidify. The crystalline solid was collected and the filtrate concentrated; ethanol was again added, and additional precipitation occurred. The crude product was recrystallized from ethanol to produce a shiny, light yellow amorphous solid (2.77 g, 50.8%), mp 114.0–114.5 °C. IR (KBr): 3008.4–3080.6, 2844.1–2932.6, 1598.9, 1490.7, 1450.2, 1436.7, 1072.6, 1003.1, 950.6, 748.5, 699.1, 690.4 cm^{-1}. ^1H NMR (Me_2SO-d_6, 300 MHz): δ 3.42 (d, 2 H, *J* = 7.1 Hz), 5.90 (dt, 1 H, *J* = 14.7, 7.1 Hz), 6.15–6.45 (m, 5 H), 6.59 (d, 1 H, *J* = 15.8 Hz), 6.97 (m, 1 H), 7.17–7.47 (m, 10 H, ArH). MS *m/e* (intensity): 272 (95.1, M^+), 181 (100.0), 166 (34.3), 155 (18.8), 142 (35.4), 129 (15.0), 115 (31.1), 103 (17.5), 91 (41.0). Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.35; H, 7.44.

1,13-Diphenyltrideca-1,3,5,7,9,11-hexaene (DP13-H). 1,13-Diphenyltrideca-1,3,5,7,9,11-hexaene was prepared analogously to DP5-H and DP9-H from trimethylenebis(triphenylphosphonium) bromide (7.26 g, 10.0 mmol) and 5-phenylpenta-2,4-dienal[36] (3.16 g, 20.0 mmol). Trituration of the resultant black tar with ethanol produced the crude product as a red-brown solid. Subsequent Soxhlet extraction of the solid, with ethanol as solvent, afforded the compound as an orange solid. Recrystallization from ethanol produced the product as a bright yellow amorphous solid (1.37 g, 42.2%), mp 188–189 °C. IR (KBr): 3008.7–3080.8, 2848.1–2956.4, 1599.4, 1491.9, 1450.8, 1438.8, 1072.4, 1006.4, 975.8, 748.6, 699.3, 690.7 cm^{-1}. ^1H NMR (after sonication, $CDCl_3$, 300 MHz): δ 3.43 (d, 2 H, *J* = 6.7 Hz), 5.85 (dt, 1 H, *J* = 14.4, 6.7 Hz), 6.09–6.43 (m, 9 H), 6.53 (d, 1 H, *J* = 15.5 Hz), 6.83 (m, 1 H), 7.15–7.40 (m, 10 H, ArH). MS *m/e* (intensity): 324 (100.0, M^+), 233

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(27.7), 167 (33.4), 155 (43.7), 129 (42.9), 115 (44.0), 91 (99.0). HRMS for $C_{25}H_{24}$: calcd 324.1878, found 324.1891.

1-(Tri-*n*-butylstannyl)-4-methoxybutadiene. In a modification of the procedure of Wollenberg,[37] a catalytic amount of 2,2′-azobis(isobutyronitrile) in a flask was heated by heat gun to dispel water. A rubber septum was added, and the flask was cooled to room temperature under a flow of argon. To the cooled flask was added *cis*-1-methoxy-1-buten-3-yne (7.39 g, 90.0 mmol, purified as according to Kraus and Frazier[38]), and after the mixture was stirred at 25 °C for 10 min, tri-*n*-butyltin hydride (26.2 g, 90.0 mmol) was added. The rubber septum was replaced by a West condenser, and the reaction was left to stir at 90 °C. After 3 h, the reaction became light brown and was left to stir an additional 12 h, after which time it was distilled under reduced pressure (<1 Torr) through a short path to yield three fractions: (1) 0.551 g (bp 96–107 °C); (2) 17.6 g (bp 107–128 °C); and (3) 9.96 g (bp 132–140 °C). Fractions 2 and 3 were shown by GC to be in excess of 97% pure. The total combined weight and GC purity indicated a total of 26.8 g (79.8%) of product.

7-Phenylhepta-2,4,6-trienal. To an amber-colored solution of 1-(tri-*n*-butylstannyl)-4-methoxybutadiene (26.2 g, 70.2 mmol) in 120 mL of tetrahydrofuran maintained at −78 °C was added *n*-butyllithium (33.5 mL of a 2.3 M hexane solution, 77.1 mmol), and the solution immediately turned dark brown to black. After the solution was stirred for 3 h at −78 °C, cinnamaldehyde (8.80 g, 67.0 mmol) in 50 mL of tetrahydrofuran was added dropwise. The reaction was left to stir at −78 °C for 5.5 h, monitoring by thin-layer chromatography (hexane/EtOAc, 4:1) until no more product formed. The reaction was quenched with aqueous $NaHCO_3$. The resulting suspension, containing some precipitate, was washed with ether and filtered, and the aqueous layer was extracted with ether (3 × 100 mL). The combined extracts were dried over K_2CO_3, filtered, and concentrated to produce a gold-yellow oil. This material containing the intermediate enol ether was used for hydrolysis to the trienal without further purification. The hydrolysis was effected by stirring the crude enol ether in 300 mL of 5% aqueous tetrahydrofuran at 25 °C in the presence of *p*-toluenesulfonic acid (0.637 g, 3.35 mmol, 5% of 67.0 mmol). The resultant yellow solution became orange after 1 h, and thin-layer chromatography (hexane/EtOAc, 4:1) indicated no further product formation after 4.5 h. The reaction was poured into a separatory funnel and extracted with ether (3 × 100 mL), and the organic extracts were dried over $MgSO_4$, filtered, and condensed to ca. 100 mL, during which time the crude product precipitated. The solid was filtered and the mother liquor condensed to a dark red oil from which orange needles formed upon cooling. Filtration of the solid and column chromatography (SiO_2; hexane/EtOAc, 4:1) of the mother liquor produced 7.67 g (62.2%) of pure aldehyde after recrystallization from benzene/hexane (1:1); mp 116.5–117.5 °C (lit.[39] mp 116.5–118 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.07 (dd, 1 H, J = 15.2, 7.9 Hz), 6.44 (dd, 1 H, J = 14.7, 11.2 Hz), 6.64–6.84 (m, with d at 6.73, 3 H, J = 13.3 Hz), 7.07 (dd, 1 H, J = 15.2, 11.2 Hz), 7.18–7.35 (m, 5 H, ArH), 9.47 (d, 1 H, J = 7.9 Hz). MS *m/e* (intensity): 184 (55.9, M^+), 155 (63.2, M^+–CHO), 128 (42.8), 115 (50.8), 91 (100.0). Both NMR and MS data were in agreement with the literature values.[39,40]

1,7-Diphenylhepta-1,3,5-triene (DP7-H). Methyltriphenylphosphonium bromide (7.14 g, 20.0 mmol) in tetrahydrofuran (100 mL) was stirred at −78 °C for 15 min, after which *n*-butyllithium (9.13 mL of a 2.3 M solution in hexane, 21.0 mmol) was added dropwise, and the mixture was stirred at −78 °C for 1 h and then allowed to warm to 0 °C with stirring until no solid was observed. The orange solution was cooled to −78 °C, and 3-bromo-1-phenyl-1-propene (4.14 g, 21.0 mmol) in 40 mL of tetrahydrofuran was added dropwise. After the solution was stirred for 1 h at −78 °C, 1.05 equiv of 2.3 M *n*-butyllithium in hexane was added. The reaction was maintained at −78 °C for 1 h, allowed to warm to 0 °C for 30 min, and cooled to −78 °C, during which time 2.78 g (21.0 mmol) of cinnamaldehyde in 40 mL of tetrahydrofuran was added dropwise. The reaction was allowed to warm to room temperature after 1 h and brought to reflux for 12 h, after which time it was quenched with 15 mL of distilled water. The solution was washed with 20 mL of 1:1 2 N sulfuric acid/hexane, and the filtrate and washings were extracted with ether (3 × 50 mL), dried over $MgSO_4$, and concentrated under reduced pressure to produce a deep orange oil. Isolation of the crude product was effected by column chromatography on alumina with hexane as eluant. The resultant green oily compound was placed in dry ice/ethanol, whereupon it solidified into colorless to pale white needles. Recrystallization from methanol produced pure 1,7-diphenylhepta-1,3,5-triene compound as colorless crystals (237 mg, 4.8%), mp 76.0–76.5 °C. IR (KBr): 3009.5–3101.9, 2831.9–2925.9, 1595.3, 1490.6, 1452.0, 1427.3, 1073.0, 1027.7, 992.9, 742.6, 697.3 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.45 (d, 2 H, J = 7.1 Hz), 5.89 (dt, 1 H, J = 14.8, 7.0 Hz), 6.14–6.34 (m, 3 H), 6.51 (d, 1 H, J = 15.6 Hz), 6.79 (m, 1 H), 7.17–7.39 (m, 10 H, ArH); MS *m/e* (intensity): 246 (65.0, M^+), 155 (100.0), 142 (30.5), 129 (18.2), 115 (20.7), 103 (3.5), 91 (31.9). The majority of the reaction product (1.75 g, 40.3% total yield) consisted of a mixture of 1,7-diphenylhepta-1,3,5-triene and 1,7-diphenylhepta-1,3,6-triene isomers on the basis of NMR triplets at δ 3.05 and 3.21 (J = 6.6 Hz) and doublets at δ 3.35 (J = 6.5 Hz), 3.40, and 3.59 (J = 7.5 Hz). GC/MS indicated the presence of at least six isomers. Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.49; H, 7.38.

1,11-Diphenylundeca-1,3,5,7,9-pentaene (DP11-H). This compound was similarly prepared as described above for DP7-H from 7-phenylhepta-2,4,6-trienal (2.90 g, 15.8 mmol), methyltriphenylphosphonium bromide (5.36 g, 15.0 mmol), and 3-bromo-1-phenyl-1-propene (3.11 g, 15.8 mmol). Approximately 100 mL of 95% EtOH was added to the oily material from the workup, and an orange solid in the black solution formed immediately. After the solid was allowed to form, it was filtered via suction, washed with 95% EtOH, and recrystallized from EtOH to produce an orange-yellow solid that was collected and dried in vacuo to yield a yellow amorphous solid (0.917 g, 20.5%), mp 150.5–151.0 °C. IR (KBr): 3008.9–3080.4, 2844.5–2933.6, 1598.1, 1490.3, 1450.9, 1436.9, 1073.0, 1004.9, 965.5, 748.3, 699.0, 690.5 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.44 (d, 2 H, J = 7.2 Hz), 5.86 (dt, 1 H, J = 14.6, 7.1 Hz), 6.10–6.39 (m, 7 H), 6.53 (d, 1 H, J = 15.6 Hz), 6.83 (m, 1 H), 7.15–7.40 (m, 10 H, ArH). MS *m/e* (intensity): 298 (100.0, M^+), 207 (29.9), 179 (14.0), 165 (19.3), 129 (29.3), 115 (23.6), 91 (98.7). Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.34; H, 7.44.

1,17-Diphenylheptadeca-1,3,5,7,9,11,13,15-octaene (DP17-H). In an analogous preparation to DP13-H, 2.95 g (16.0 mmol) of 7-phenylhepta-2,4,6-trienal was added to the bis(ylide) generated from 5.45 g (7.59 mmol) of trimethylenebis(triphenylphosphonium) bromide at −78 °C. After reflux (14 h) and water quench, a dark brown solution containing a white precipitate resulted. Filtration of the white solid and concentration of the filtrate resulted in the formation of a black oil. Addition of ethanol, filtration of the resultant reddish brown solid, and ethanol wash resulted in a red solid that was dried in an Abderhalden drying apparatus. Recrystallization from 1:1 EtOH/THF afforded DP17-H as an orange solid (1.19 g, 42.2%), mp 239–241 °C. IR (KBr): 3008.7–3080.9, 2849.3–2940.3, 1594.5, 1492.5, 1451.6, 1426.8, 1073.0, 1007.8, 984.4, 745.5, 697.5, 689.7 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.43 (d, 2 H, J = 6.9 Hz), 5.85 (dt, 1 H, J = 14.7, 7.0 Hz), 6.09–6.42 (m, 13 H), 6.54 (d, 1 H, J = 15.7 Hz), 6.84 (m, 1 H), 7.15–7.44 (m, 10 H, ArH). MS *m/e* (intensity): 376 (78.8, M^+), 178 (17.9), 167 (24.8), 155 (25.7), 141 (26.7), 129 (39.3), 117 (43.2), 115 (39.8), 91 (100.0). HRMS for $C_{29}H_{28}$; calcd 376.2191, found 376.2189.

(Diphenylmethyl)potassium (DP1-K$^+$).[5,41] **A. Without 18-Crown-6.** Potassium (methylsulfinyl)methide (ca. 0.3 mL of a 1.5 M solution of Me_2SO-d_6) was added to diphenylmethane (47.4 mg, 0.282 mmol) in 0.5 mL of Me_2SO-d_6 in a 5-mm NMR tube, producing an orange solution. ^1H NMR (400 MHz, Me_2SO-d_6): δ 4.24 (s, 1 H), 5.63 (t, 2 H, J = 6.9 Hz), 6.41 (m, 4 H), 6.54 (m, 4 H). Deuterium exchange of the C-1 proton prevented ^{13}C and ^1H assignment. Me_2SO-h_6 (0.3 mL) was added, which allowed identification of the singlet at δ 4.24.

B. With 18-Crown-6. To a solution of diphenylmethane (27.4 mg, 0.163 mmol) in Me_2SO-d_6 (0.2 mL) and 18-crown-6 (0.4 mL of a 2.6 M solution in Me_2SO-d_6) in a 5-mm NMR tube was added 0.3 mL of the dimsylpotassium solution. Me_2SO-h_6 was then added as described above. ^{13}C chemical shifts were identical with the shifts of the sample previously described.

Procedure for DP3, DP5, and DP7. A typical procedure was as follows: A 0.10–0.40-mmol sample of the neutral hydrocarbon was dissolved in ca. 0.6 mL of Me_2SO-d_6 in a 5-mm NMR tube, and 0.1–0.3 mL of 1.5 M dimsylpotassium was added to form a dark red to blue-black solution. Upon recording the ^1H and ^{13}C spectra, we added a multimolar excess of the 18-crown-6 solution, and the NMR spectra were similarly recorded. In all cases the spectra were identical for the corresponding compounds before and after addition of crown ether. Different samples were prepared for the COSY and HETCOR spectra utilizing higher

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Table I. Chemical Shifts of Even Diphenylpolyenes

DP*N*	C-1	C-2	C-3	C-4	ipso	ortho	meta	para
2	128.4				137.0	126.4	128.7	127.6
4	132.6	129.4			137.0	126.3	128.7	127.6
6	132.4	129.3	133.8		137.0	126.3	128.7	127.6
8	132.4	129.4	133.7	133.6	137.1	126.3	128.7	127.6

concentrations without crown ether. The spectral data were as follows:

(1,3-Diphenylpropenyl)potassium ($DP3^-K^+$). ^{1}H NMR: (*E,E* conformer) δ 4.64 (d, 2 H, *J* = 13.2 Hz), 5.97 (t, 2 H, *J* = 6.9 Hz), 6.54 (m, 4 H), 6.68 (m, 4 H), 7.12 (br s, 1 H); (*E,Z* conformer) δ 5.16 and 4.28 (d, 2 H, *J* = 14.3 and 10.3 Hz), 6.05 and 6.17 (t, 2 H, *J* = 6.9 Hz), 6.60 and 6.84 (m, 9 H).

(1,5-Diphenylpentadienyl)potassium ($DP5^-K^+$). ^{1}H NMR δ 4.85 (d, 2 H, *J* = 14.4 Hz), 4.95 (m, 1 H), 6.21 (t, 2 H, *J* = 6.7 Hz), 6.60–6.75 (m, 10 H) [lit.[34] ^{1}H NMR (ether, Li^+): δ 4.81 (t, 1 H, *J* = 11.2 Hz), 5.20 (d, 2 H, *J* = 14.4 Hz), 6.22–7.62 (m, 12 H)].

(1,7-Diphenylheptatrienyl)potassium ($DP7^-K^+$). ^{1}H NMR: δ 5.03 (t, 2 H, *J* = 11.9 Hz), 5.13 (d, 2 H, *J* = 14.4 Hz), 6.26 (t, 1 H, *J* = 12.7 Hz), 6.42 (t, 2 H, *J* = 7.1 Hz), 6.62 (dd, 2 H, *J* = 13.9, 11.8 Hz), 6.80 (m, 4 H), 6.88 (m, 4 H).

(1,9-Diphenylnonatetraenyl)potassium ($DP9^-K^+$). To a 10-mm NMR tube were added 24.9 mg (0.091 mmol) of DP9-H and ca. 3.0 mL of Me_2SO-d_6. All of the compound would not go into solution until subjected to brief (5-min) sonication. The dimsylpotassium (ca. 0.4 mL of a 1.5 M solution in Me_2SO-d_6) was then added, and the spectra were recorded. ^{1}H NMR: 5.08 (t, 1 H, *J* = 12.2 Hz), 5.20 (t, 2 H, *J* = 12.2 Hz), 5.38 (d, 2 H, *J* = 14.4 Hz), 6.22 (t, 2 H, *J* = 12.5 Hz), 6.59 (t, 2 H, *J* = 6.7 Hz), 6.67 (dd, 2 H, *J* = 14.4, 11.7 Hz), 6.93–6.99 (m, 8 H). The spectrum was unchanged upon addition of ca. 0.5 mL of 2.6 M 18-crown-6 in Me_2SO-d_6.

(1,11-Diphenylundecapentaenyl)potassium ($DP11^-K^+$). Dimsylpotassium (0.5 mL of a 2.5 M solution in Me_2SO-d_6) was added to 3 mL of Me_2SO-d_6 containing 28.2 mg (0.094 mmol) of DP11-H in a 10-mm NMR tube. The mixture was transferred via gas-tight syringe and filtered directly into a second 10-mm NMR tube through a 5-μm filter. ^{1}H NMR: δ 5.17 (t, 2 H, *J* = 12.0 Hz), 5.37 (t, 2 H, *J* = 12.0 Hz), 5.58 (d, 2 H, *J* = 14.8 Hz), 6.16 (m, 1 H), 6.23 (t, 2 H, *J* = 12.4 Hz), 6.74 (m, 4 H), 7.04–7.45 (m, 8 H).

(1,13-Diphenyltridecahexaenyl)potassium ($DP13^-K^+$). The anion was generated from 17.4 mg (0.054 mmol) of DP13-H in 3 mL of Me_2SO-d_6 and 0.5 mL of 2.5 M dimsylpotassium in a 10-mm NMR tube. As in the previous example, filtration was required to provide an acceptable sample. ^{1}H NMR: δ 5.22 (m, 1 H), 5.29 (t, 2 H, *J* = 11.7 Hz), 5.52 (t, 2 H, *J* = 12.3 Hz), 5.75 (d, 2 H, *J* = 15.0 Hz), 6.16 (m, 2 H), 6.25 (t, 2 H, *J* = 12.6 Hz), 6.75 (dd, 2 H, *J* = 14.4, 11.7 Hz), 6.81 (m, 2 H), 7.02–7.48 (m, 8 H).

Procedure for DP2, DP4, DP6, and DP8. A typical procedure is as follows: A 0.10–0.30-mmol sample of the hydrocarbon was dissolved in 1.0–1.5 mL of Me_2SO-d_6 in a 5-mm NMR tube. ^{13}C chemical shifts were determined from the HETCOR spectrum utilizing DP6 as a representative sample. The results are reported in Table I.

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^{1}H NMR Resonance Assignment of the Active Site Residues of Paramagnetic Proteins by 2D Bond Correlation Spectroscopy: Metcyanomyoglobin

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Abstract: Two-dimensional conventional magnitude COSY, phase-sensitive pure absorption DQF-COSY, and HOHAHA experiments have been successfully applied to paramagnetic low-spin ferric sperm whale metcyanomyoglobin to identify the spin systems of the side chains of the residues located in the heme cavity. The assignments from the present bond correlation spectroscopy for the residues of Ile FG5/99, Phe CD1/43, His F8/93, Val E11/68, and heme itself confirm the assignments made previously by interpreting nuclear Overhauser effect, NOE, data on the basis of the X-ray crystal structure. The spin system of a Leu side chain with strongly hyperfine shifted resonances has been unambiguously identified with a combination of COSY and HOHAHA spectra and assigned to the Leu F4/89 residue located in the heme pocket on the proximal side, for which the initial partial assignments are shown to be invalid. The incorrect earlier assignments resulted from a difference between the solution and crystal orientation of the side chain. Molecular modeling and dipolar shift calculations upon rotating the Leu F4/89 side chain about the C_β–C_γ bond by ~120° lead to an orientation consistent with both the observed dipolar shifts and NOEs to the heme. The methods of bond correlation spectroscopy are qualitatively evaluated and shown to be able to identify cross peaks from pairs of protons experiencing very rapid paramagnetic relaxation rates with T_1s as short as ~20 ms and line widths as large as ~100 Hz. Preliminary 2D bond correlation spectroscopic data on the cyano complex of horseradish peroxidase suggest that *J* cross peaks can identify residues in even larger paramagnetic heme proteins. The various methods considered, however, differ significantly in their information content, with the magnitude COSY map providing the optimal information on the strongly relaxed protons. In particular, the double quantum filter is found to strongly discriminate against rapidly relaxed, broad, and spin-coupled resonances, making DQF-COSY experiments virtually useless for the protons closest to the iron. The variable-temperature HOHAHA and COSY maps serve to define complete spin systems. Therefore, it is clear that 2D bond correlation spectroscopy can be profitably applied to paramagnetic macromolecules and that, along with the 2D nuclear Overhauser effect spectroscopy (NOESY) [Emerson, S. D.; La Mar, G. N. *Biochemistry* **1990**, *29*, 1545–1556], the solution structures of paramagnetic molecules, at least low-spin ferric molecules, should be determinable with 2D NMR techniques in a fashion now attainable for diamagnetic molecules.

Introduction

It has long been recognized that the information content of the ^{1}H NMR spectra of paramagnetic proteins is very high, but the needed resonance assignments and interpretative basis of the hyperfine shifts are much more complicated than for diamagnetic proteins.[1-7] Originally, it was thought that 2D NMR methods used for diamagnetic molecules[8] will have little applicability to

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