metastable solutions precipitate lithium metal to yield dilute stable solutions in the mixed solvent systems. Similarly, a solution of $Li(CH_3NH_2)_4$ and sodium was initially soluble in DEE but yielded a light blue solution together with precipitated metal(s) upon standing or upon the addition of excess DEE. In addition to sodium metal, rubidium metal also dissolved in a solution of $Li(CH_3NH_2)_4$ to produce a dark blue solution. By analogy with the corresponding solutions of lithium and sodium, it is presumed that the solution contains the species $Li^+(CH_3NH_2)_4$ and Rb^-.

The results described in this paper suggest that lithium, without or with sodium, plus a simple amine such as methylamine or ethylenediamine[24] might provide useful homogeneous reducing agents in various solvents, but such applications have not yet been explored. There is, of course, a vast literature that deals with reductions by active metals such as metal–ammonia and metal–amine solutions,[25,26] solvated metal atoms,[27] and aromatic radical anions.[28] The present work would add to this list relatively concentrated solutions that contain either electrons (solvated or metallic) or the sodide anion, Na^-. This could prove to be useful in reduction reactions in which either one-electron or two-electron reducing agents are needed. It also provides the opportunity to study concentrated alkali metal solutions in other solvents than methylamine and ammonia. Preliminary results show that the other alkali metals can also be solubilized by using $Li(CH_3NH_2)_4$.

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^{13}C NMR Spectroscopy of α,ω-Diphenylpolyenyl Anions. Confirmation of Charge Localization in Soliton Model Compounds

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The notion that delocalization in ostensibly "infinite" polyacetylene chains treated with π-donors or acceptors only extends over a limited domain has been one of the more controversial aspects of the soliton theory. According to this theory,[1] electrical conductivity in such systems is due to the presence of mobile charged defects ("solitons") which are described in terms appropriate for a resonance-delocalized carbanion with a conjugation length of approximately 31 CH units or, more precisely, a full width at half height of 15 CH units. Inasmuch as charge density in short polyenyl anions, e.g., pentadienyl anions, is known to be higher at the central carbon,[2] the extent to which charge accumulates in longer polyenyl anions provides an important reference point between the solid-state physics of one-dimensional conductors and the organic chemistry of resonance-stabilized anions.

Our reference molecules were the linear odd-alternant α,ω-diphenylpolyenyl anions ($Ph(CH)_nPh^-$, $n = 1, 3, 5, 7, 9, 11, 13$), to which we refer in shorthand notation as DP1, DP3, DP5, etc. Phenyl-terminated anions were chosen for their stability and ease of preparation as well as for their utility for estimating delocalization; that is, at what point does negative charge cease to delocalize into the aromatic rings? The Dewar nonbonded molecular orbital (NBMO) formalism[3] predicts, at the Hückel level, even distribution of negative charge at the odd-numbered carbon atoms and zero charge (nodes) at the even carbons. In contrast, the SSH theory,[1] a modified Hückel treatment reminiscent of the "ω" bond-order approach,[4] predicts accumulation of charge at the central carbon atoms, again with nodes at even carbons. Less intuitively, the Boudreaux, Chance, Brēdas, Silbey (BCBS) modification of the soliton theory,[5] based upon an MNDO method, predicts charge alternation, with even atoms possessing positive charge as a result of charge polarization by the negatively charged odd centers. We have been able to resolve this issue by an appeal to the Spiesecke–Schneider correlation[6] of charge density with ^{13}C chemical shift.

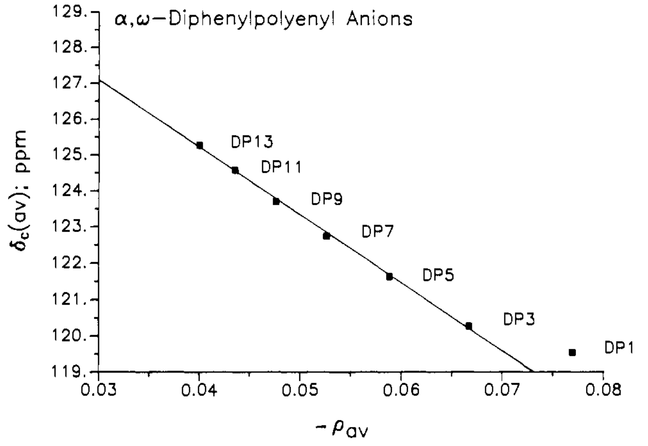

Figure 1. Average ^{13}C chemical shift vs average charge density for diphenylpolyenyl anions.

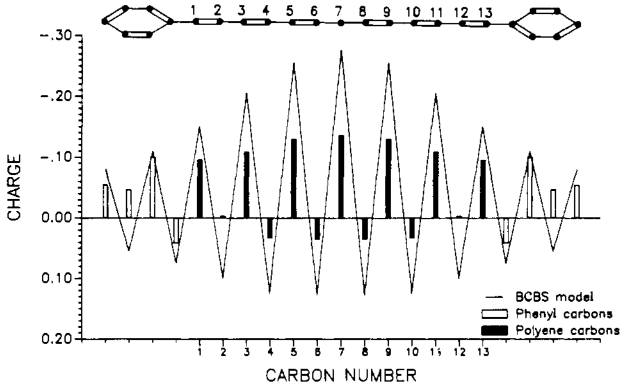

Figure 2. Histogram of charge density vs carbon number for DP13.

The required diphenylpolyenyl anions were generated in dimethyl sulfoxide solution by deprotonation of the corresponding carbon acids with potassium methylsulfinylmethide in dimethyl sulfoxide, a solvent which avoids ion pairing and other spectroscopic complications. The hydrocarbons themselves were generated by straightforward Wittig methodology[7] and presented no special complications apart from an increasing insolubility with chain length, which prevented ^{13}C NMR spectral assignments for

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Table I. Chemical Shift and Charge Densities

DPN N =	C1	C2	C3	C4	C5	C6	C7	ipso	ortho	meta	para
	chemical shift (δ)										
1	80.4							145.2	116.2	127.7	105.9
	(−0.279)							(0.067)	(−0.091)	(−0.026)	(−0.143)
3	90.2	127.9						145.4	117.5	128.1	111.3
	(−0.227)	(−0.026)						(0.068)	(−0.081)	(−0.025)	(−0.114)
5	96.5	134.6	98.2					143.9	119.4	128.0	115.0
	(−0.193)	(0.010)	(−0.184)					(0.058)	(−0.071)	(−0.025)	(−0.095)
7	102.4	133.7	101.5	140.5				142.7	120.8	128.1	117.7
	(−0.163)	(0.005)	(−0.167)	(0.042)				(0.053)	(−0.064)	(−0.025)	(−0.080)
9	107.4	133.2	105.4	139.8	103.3			141.7	121.9	128.2	119.7
	(−0.135)	(0.003)	(−0.146)	(0.038)	(−0.157)			(0.048)	(−0.058)	(−0.024)	(−0.069)
11	111.5	132.7	109.1	139.2	105.9	139.6		140.9	122.8	128.3	121.3
	(−0.113)	(0.000)	(−0.126)	(0.035)	(−0.143)	(0.037)		(0.044)	(−0.053)	(−0.023)	(−0.061)
13	114.9	132.3	112.5	138.6	108.6	139.0	107.5	140.3	123.4	128.3	122.5
	(−0.095)	(−0.002)	(−0.108)	(0.032)	(−0.129)	(0.034)	(−0.135)	(0.041)	(−0.050)	(−0.023)	(−0.054)

DP17. Surprisingly, the anions themselves exhibited no special tendency toward conformational diversity, despite the increasing availability of Z conformations with chain length. Indeed, ^1H NMR coupling constants were consistent with the all trans conformations for chains longer than C3. Homonuclear 2D (COSY) NMR spectroscopy allowed unambiguous assignment of proton chemical shifts in all cases, and heteronuclear ^{13}C–^1H NMR spectroscopy thus allowed indirect assignment of ^{13}C chemical shifts. Linear least-squares treatment of the average charge density vs ^{13}C chemical shift (see Figure 1), excluding DP1, gave excellent statistics and allowed a calculation of individual charge densities at each site from the formula

$$\rho_C = (\delta_C - 132.7)/187.3 \qquad (1)$$

The assigned chemical shifts and calculated charge densities are shown in Table I.[8,9] More illustrative are these results plotted in histogram form. Figure 2 indicates the results for DP13. Included for the purpose of comparison are results from the calculated BCBS soliton model. As can clearly be seen, despite the delocalization that one might anticipate into the phenyl groups, negative charge accumulates in the center of the chain away from the ostensibly stabilizing phenyl groups. However, the diminution of charge with distance is less than that predicted by the 15 CH half-width of the SSH model but closer to that predicted by BCBS. Our solubility limitations prevent us from extrapolation to the limiting "true" soliton width. Although the amplitude of charge alternation in the phenyl-substituted anion is not as large as in the BCBS model, charge alternation remains a significant feature.

Although mechanisms for soliton generation and propagation are still under intense scrutiny, the predicted accumulation of charge within a fixed conjugation length thus appears to be validated by examination of resonance-stabilized carbanion models, even in a solvent, dimethyl sulfoxide, which minimizes counterion effects.[10] The SSH Hamiltonian, a one-electron treatment, does not predict the charge alternation readily rationalized by multiconfigurational methods and now verified by ^{13}C nuclear magnetic resonance. However, its success at predicting the general structure as well as optical and magnetic properties of conducting polymers must be viewed as a vindication of one-dimensional calculational methods.

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Synthesis and Characterization of a Soluble Oxide Inclusion Complex, $[CH_3CN\subset(V_{12}O_{32}^{4-})]$

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Microporous oxides such as zeolites have attracted widespread attention due to their ability to reversibly absorb small covalent molecules in a size- and shape-selective fashion.[2] The specificity associated with this inclusion phenomenon arises in part from the structural rigidity of the oxide host frameworks involved that impose correspondingly rigid geometric constraints on the guest molecules absorbed. To date, no molecular analogues of these solid oxide inclusion compounds have been reported, a surprising state of affairs given the existence of a wide variety of molecular inclusion complexes based on organic host molecules.[3]

The dodecavanadate inclusion complex $[CH_3CN\subset(V_{12}O_{32}^{4-})]$ is prepared as a dark red, crystalline, tetra-*n*-butylammonium salt in >80% yield by refluxing an acetonitrile solution of $V_{10}O_{28}H_2[(n\text{-}C_4H_9)_4N]_4$ for 1–2 min, adding sufficient diethyl ether to obtain a precipitate, and recrystallizing the precipitate from 1:2 V/V acetonitrile/ethyl acetate at −5 °C. Although crystalline $[CH_3CN\subset(V_{12}O_{32}^{4-})][(n\text{-}C_4H_9)_4]_4$,[4] **1**, is unsuitable for X-ray structural analysis, suitable crystals of a solvated tet-

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(4) IR (Nujol, 500–1000 cm^{-1}) 524 (w), 551 (w), 611 (sh), 658 (vs), 714 (s), 758 (vs), 791 (sh), 861 (s), 994 (vs); ^{51}V NMR (0.02 M, 25 °C, CH_3CN) δ −590 (4V), −598 (4V), −606 (4V) relative to external $VOCl_3$. Anal. Calcd for $C_{66}H_{147}N_5V_{12}O_{32}$: C, 37.14; H, 6.94; N, 3.28; V, 28.64. Found: C, 37.15; H, 6.94; N, 3.31; V, 28.59.