Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

^{13}C NMR Evidence for a Fixed Soliton Width in Anionic Polyacetylene

L. M. Tolbert [a] & M. E. Ogle [a]
[a] School of Chemistry, Georgia Institute of Technology, Atlanta, GA, 30332-0400
Version of record first published: 22 Sep 2006.

To cite this article: L. M. Tolbert & M. E. Ogle (1990): ^{13}C NMR Evidence for a Fixed Soliton Width in Anionic Polyacetylene, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 189:1, 279-286

To link to this article: http://dx.doi.org/10.1080/00268949008037240

Mol. Cryst. Liq. Cryst., 1990, Vol. 189, pp. 279–286
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

^{13}C NMR Evidence for a Fixed Soliton Width in Anionic Polyacetylene

L. M. TOLBERT† and M. E. OGLE

School of Chemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400

According to the Su, Schrieffer, and Heeger (SSH) theory, the charge carrier in doped polyacetylene is a charged soliton of finite half-width with maximum charge at the center of the defect. The classical organic chemistry counterpart of the *n*-type soliton is an odd-alternate resonance-stabilized polyenyl anion, whose charge distribution is described by the coefficients of the occupied non-bonding molecular orbital. Examination of the nuclear magnetic resonance properties of α,ω-diphenylpolyenyl anions, which are models for anionic polyacetylene oligomers, has confirmed the existence of charge localization in resonance-stabilized polyenyl anions allows us to estimate the soliton width as 26 carbon atoms in *n*-doped polyacetylene.

INTRODUCTION

According to the theory as developed by Su, Schrieffer, and Heeger, the charge carrier in reductively (or oxidatively) doped polyacetylene is a negatively or positively charged soliton of finite half-width with maximum charge at the center of the defect, zero amplitude at every other carbon atom, and diminishing amplitude away from the center[1] (see Figure 1). This soliton has its counterpart in classical organic chemistry, and the *n*-type soliton may be associated with a resonance-stabilized polyenyl anion, a member of the general class of odd alternant hydrocarbons anions. A feature of such anions is the existence of a highest occupied non-bonding molecular orbital (HOMO) whose atomic orbital coefficients describe the charge density in the system. Although in the Hückel approximation these coefficients are equal in magnitude but alternating in sign, higher level treatments provide similar predictions about the charge density distribution. In fact, 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 on proton magnetic resonance spectra.[2] However, no anions have been prepared which allow confirmation of the prediction that such systems have a finite conjugation width. The existence of a finite conjugation width is an essential com-

†To whom all correspondence should be addressed.

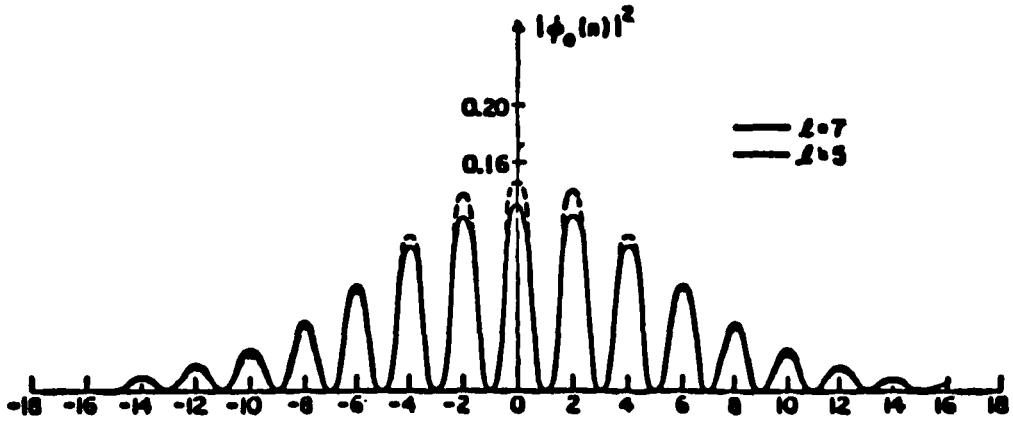


FIGURE 1 SSH model for soliton in polyacetylene. Reprinted with permission from Reference 1b.

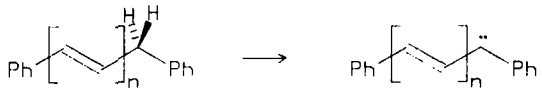
is an essential component of soliton mobility. Thus we embarked on a program to address the problem from an organic chemist's perspective, synthesizing polyenyl anions of known length and testing the convergence of their spectroscopic properties with increasing chain length. In the limit, these properties should correspond to those of doped polyacetylene.

Our initial efforts have concentrated on α,ω-diphenylpolyenyl anions, using as our main analytical technique ^{13}C-nmr spectroscopy.[3] Several years ago Spiesecke and Schneider observed that for planar symmetrical hydrocarbon ions, charge density and ^{13}C chemical shift were correlated[4] (see Equation 1). O'Brien generalized this treatment to nonsymmetrical systems[5] provided sufficient numbers of examples were available to generate good linear least squares statistics. Determination of the fitting coefficients for the average chemical shift δ_{av} vs. average charge density ρ_{av} would allow calculation of the charge density at individual carbon atoms from the ^{13}C chemical shift (see Equation 2). This 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.

$$\delta_c = \alpha\rho_c + \delta_0 \tag{1}$$

$$\delta_{av} = \alpha\rho_{av} + \delta_0 \tag{2}$$

Generation of Anions. Our method required access to the odd-numbered diphenylpolyenes which were synthesized through standard Wittig methodology with some modifications.[6] Synthesized for these purposes were 1,3-diphenylpropene (**DP3-H**), 1,5-diphenylpentadiene (**DP5-H**), 1,7-diphenylheptatriene (**DP7-H**), 1,9-diphenylnonatetraene (**DP9-H**), 1,11-diphenylundecaptentaene (**DP11-H**), and 1,13-diphenyltridecahexaene (**DP13-H**). Diphenylmethane (**DP1-H**) was obtained commercially. Dimethyl sulfoxide solutions of the hydrocarbon precursors were treated with potassium methylsulfinylmethide ("dimsyl")[7] to form deeply colored solutions which ranged from orange to deep blue-black as the chain length increased. The



n = 1, 2, 3, 4, 5, 6, 7, 8 ....

FIGURE 2 Generation of α,ω-diphenylpolyenyl anions.

higher homologues were poorly soluble, and the solutions were filtered under argon atmosphere to obtain homogeneous solutions for spectroscopic analysis. In the case of **DP17** and higher homologues, anisotropic line broadening prevented acquisition of analyzable spectra. However, all anions **DP1** through **DP13** yielded quite satisfactory ^{13}C and ^{1}H spectra for further analysis (see Table I).

Assignment of ^{13}C chemical shifts for the anions presented some ambiguities, although qualitatively the carbon atoms bearing formal negative charge had chemical shifts upfield of 115 ppm. Thus it was necessary to use two-dimensional (COSY) spectroscopy to assign the proton absorptions first, and from these to assign the ^{13}C chemical shifts from the heteronuclear (HETCOR) two-dimensional spectrum. A representative ^{13}C spectrum for **DP9** is shown in Figure 3.

With the ^{13}C chemical shifts in hand, we were able to apply the O'Brien method. A plot of average charge density vs. average chemical shift gave an excellent linear least squares fit to the equation

$$\delta_c = 187.3\rho_c + 132.7$$

provided the first member of the series **DP1** was neglected (see Figure 4). The failure of this anion to follow the Spiesecke-Schneider equation was perhaps a reflection of nonplanarity in this anion, which causes mixing of low-lying n-π^* states.[8]

A plot of the higher members of the series in histogram form indicates that the charge densities do indeed indicate localization in the center of the charged polyene (e.g. DP 13, see Figure 5), although substantial charge alternation is more in line with higher level calculations, e.g., the Brèdas, Chance, Boudreaux, Silbey (BCBS) model.[9]

We now turn our attention to the perhaps most critical issue of the soliton theory, that is, what is the soliton width? One approach to the solution is to view the phenyl group as a reporter group for the charge density at the terminus of the polyene chain. Extrapolation to infinite chain length should thus allow us to predict the limiting chemical shifts. In fact, a plot of chemical shift vs. $1/N$, where N is the total carbon number, is linear for ortho, meta, para, ipso, and α carbon atoms for all anions higher than **DP3** and allows us to make such an extrapolation. Figure 6 displays the chemical shifts and the least-squares first order lines which project to the y axis. We now compare to **DPN** anions with analogous neutral compounds, namely, the α,ω-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**),

TABLE I

Chemical shifts of diphenylpolyenyl anions

	C1	C2	C3	C4	C5	C6	C7	ipso	ortho	meta
3	80.4	—	—	—	—	—	—	145.2	116.2	127.7
5	89.8	127.9	—	—	—	—	—	145.4	117.5	128.0
7	96.5	134.6	98.2	—	—	—	—	143.9	119.4	128.0
9	102.4	133.7	101.5	140.5	—	—	—	142.7	120.8	128.1
11	107.4	133.2	105.4	139.8	103.3	—	—	141.7	121.9	128.2
13	111.5	132.7	109.1	139.2	105.9	140.1	—	140.9	122.8	128.3
	114.9	132.3	112.5	138.6	108.6	139.0	107.5	140.3	123.4	128.3

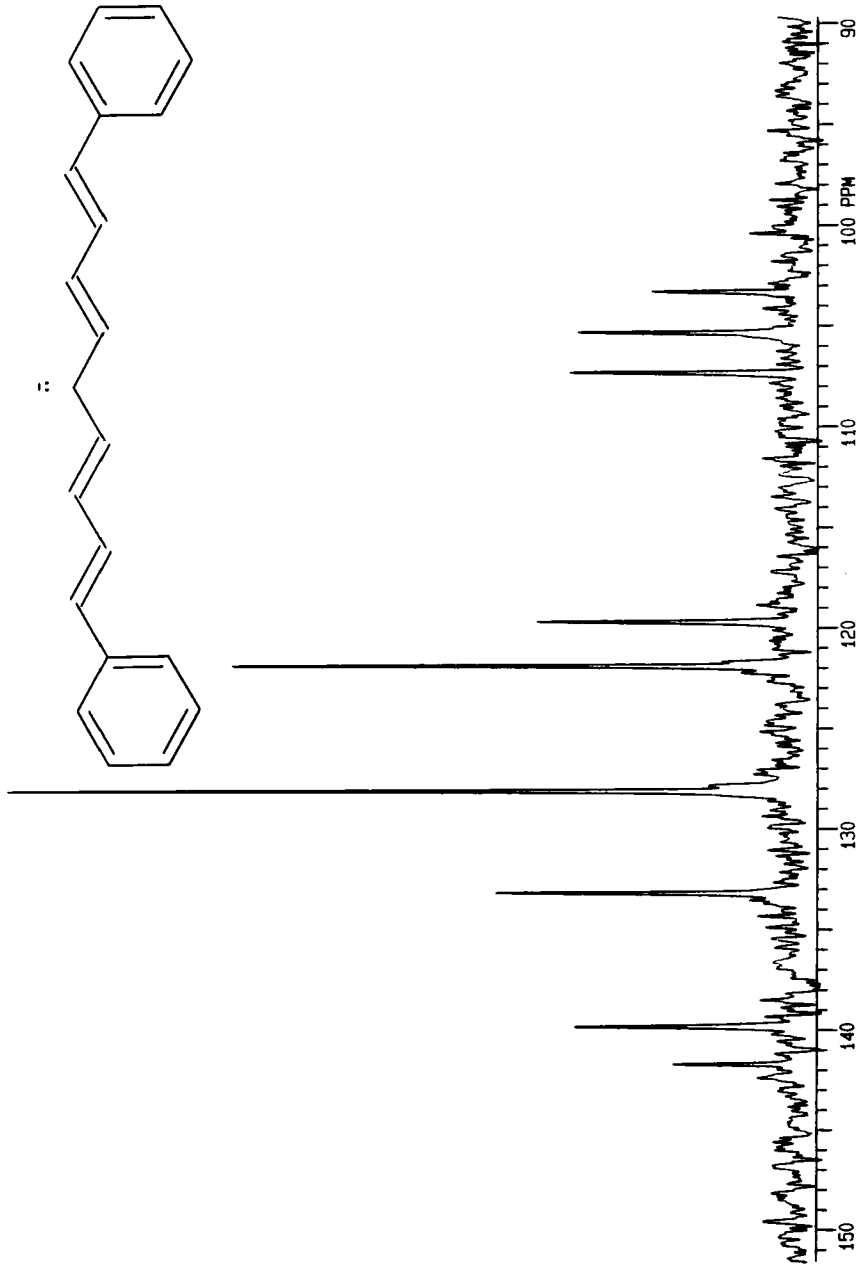


FIGURE 3 ^{13}C-NMR spectrum of 1,9-diphenylnonatetraenyl anion.

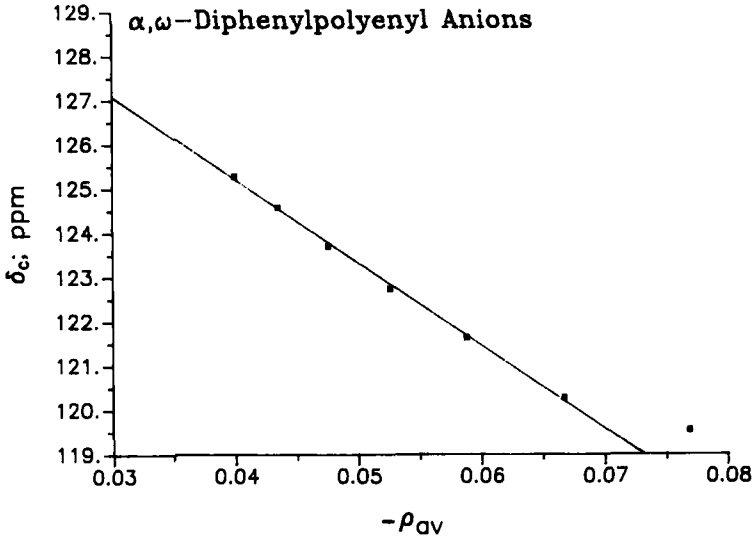


FIGURE 4 Charge density vs. chemical shift correlation.

to determine the limiting ^{13}C chemical shifts. Determination and assignment of the ortho, meta, para, ipso, and α ^{13}C chemical shifts by two-dimensional spectroscopy provides the interesting result that these shifts are independent of chain length after **DP2** and allow us to conclude that these shifts also correspond to the chemical shift of the hypothetical α,ω-diphenylpolyene of infinite length.

Finally, we consider the point at which the two sets of chemical shifts converge. For 1,8-diphenyl-1,3,5,7-tetraene, the chemical shifts for the *alpha, meta, ortho,*

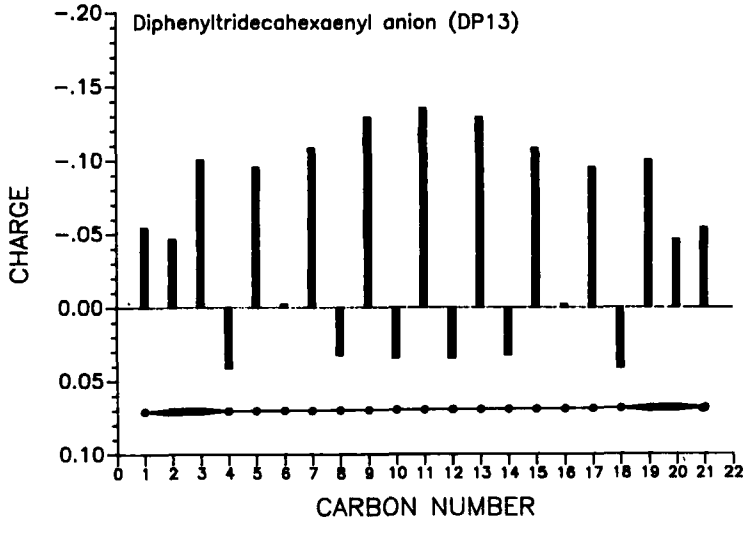


FIGURE 5 Charge-density distribution in 1,13-diphenyltridecahexaenyl anion (**DP13**).

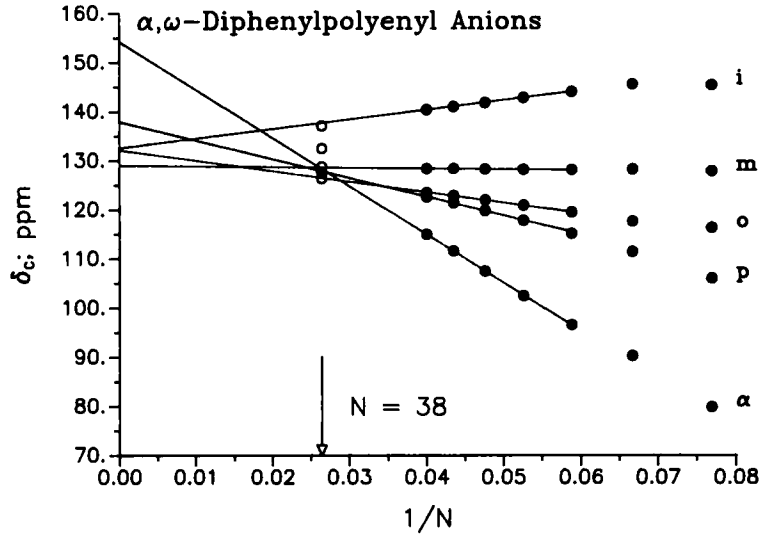


FIGURE 6 Chemical shift vs. chain length.

para, and *ipso* carbon atoms are 132.4, 128.7, 126.3, 127.6, 137.1 ppm, resp. There is a point at which the lines for the aromatic carbon atoms obtained from Figure 6 intersect, namely at $1/N = .0264$, i.e., $N = 38$. Since this number includes the two phenyl groups, as well we subtract 12 to obtain the extrapolated soliton width of ca.26. Inclusion of this point in Figure 6 illustrates convergence of the two experimental sets of data and provide confidence that we have actually measured the soliton width.

According to theory,[1] it is appropriate to speak of the half-width at half height of a soliton, which is ca. 15 carbon atoms for polyacetylene. Non-zero coefficients extend for some distance from the soliton center. Nonetheless, there is a practical limit to such delocalization, as an examination of the magnitude of coefficients in Figure 1 illustrates, of ca. 31 carbon atoms. Our experimentally determined value is in gratifying agreement with this prediction.

Acknowledgment

Support of this research by the U.S. Department of Energy is gratefully acknowledged.

References

1. (a) W. P. Su, J. R. Schrieffer and A. J. Heeger, *Phys. Rev. Lett.*, **42**, 1698 (1979). (b) W. P. Su, J. R. Schrieffer and A. J. Heeger, *Phys. Rev. B*, **22**, 2099 (1980). (c) W. P. Su, in "Handbook of Conducting Polymers," T. J. Skotheim, ed., Marcel Dekker, New York, 1986, pp. 757–794.
2. (a) H. Kloosterziel and M. A. Werner, *Recl. Trav. Chim. Pays-Bas*, **94**, 124 (1975). (b) H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **93**, 215 (1974) and references therein.
3. For previous results, see L. M. Tolbert and M. E. Ogle, *J. Am. Chem. Soc.*, 1989, **111**, 5958. See

also L. M. Tolbert and M. E. Ogle, *Ibid.*, in press.
4. H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).
5. D. H. O'Brien, A. J. Hart and C. R. Russell, *J. Am. Chem. Soc.*, **97**, 4410 (1975).
6. G. Wittig, H. Eggers and P. Duffner, *Annalen*, **619**, 10 (1958).
7. W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum and N. R. Vanier, R. *J. Am. Chem. Soc.*, **97**, 7006 (1975).
8. T. Tokuhiro and G. Fraenkel, *J. Am. Chem. Soc.*, **91**, 5005 (1969).
9. D. S. Boudreaux, R. R. Chance, J. L. Brèdas and R. Silbey, *Phys. Rev. B.*, **28**, 6927 (1983).