Equilibrium Acidities of Some α,ω-Diphenylpolyenes[1]

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Received May 24, 1993. Revised Manuscript Received November 9, 1993[•]

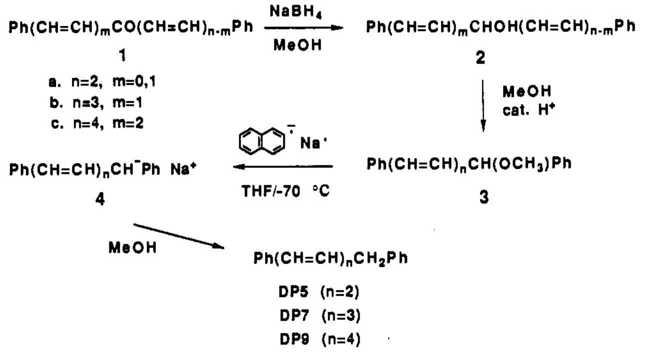
Abstract: Cesium ion pair acidities were measured in THF for a series of diphenylmethane vinylogues that form α,ω-diphenylpolyenyl anions with linearly conjugated chains of 3–9 carbon atoms. The dissociation constants of the diphenylpolyenyls in THF were determined by UV–vis spectroscopy and are rationalized with an electrostatic model. Acidity and dissociation data were combined with measurements of stereoisomer equilibria to estimate the differences in delocalization energy among the diphenylpolyenyl ions. The experimental differences in acidity correlate well with AM1 and molecular mechanics (MMPI) calculations.

Introduction

To our knowledge there has been no systematic study of the equilibrium acidity of polyenes as a function of chain length. Such a study could be useful in characterizing the properties of polyacetylene anions or solitons[3] and on the resonance energies of linearly conjugated carbanions.[4] The simple polyene carbanions are expected to be difficult to study because their basicities are too high and ion pair aggregation may be important. Allyllithium, for example, is partially aggregated in tetrahydrofuran (THF).[5] Accordingly, we chose to study the corresponding α,ω-diphenylpolyenes and report here our results for the equilibrium acidities in THF of the first four members, Ph(CH=CH)$_n$CH$_2$Ph (n = 1, DP3; n = 2, DP5; n = 3, DP7; n = 4, DP9).

The lithium salt of 1,3-diphenylpropene (DP3$^-$Li$^+$) has been studied extensively. UV–vis spectroscopy and NMR studies have shown this salt to be present almost entirely as solvent-separated or loose ion pairs (SSIP) in THF at room temperature and below.[6–8] The allylic system is present mostly as the *E,E*-conformer, but at room temperature, about 8% of the *E,Z*-isomer is also present;[9–13] the *cis–trans* isomerism is readily accomplished photochemically as well as thermally.[14–16] The potassium salt of DP3 has been shown to be >99% contact ion pairs (CIP) in THF at 20 °C.[7c] The lithium salts of DP5 and DP7 have been shown to be almost entirely SSIP in THF.[17] The ^{13}C NMR spectra of the free carbanions in DMSO have been reported.[3a]

Scheme 1



In this study we present ion pair proton-transfer equilibrium constants for the cesium salts of DP3–9 in THF. These salts are shown to be monomeric contact ion pairs, but their dissociation constants to the free carbanions were determined by UV–vis spectroscopy. The relative energies of these carbanions are compared with some semiempirical MO calculations.

Results and Discussion

Synthesis of Diphenylpolyenes. The synthesis of the diphenylpolyenes reported by Parkes and Young[17] gave mixtures that could not be separated completely. Syntheses of these hydrocarbons were also reported by Tolbert and Ogle.[3a] They used Wittig reactions, and some of the products apparently were mixtures. We followed the general method of Hafner and Goliasch[18] (Scheme 1). The ketones **1**, which are easily prepared by aldol condensation, were reduced to the alcohols **2** and further converted to the methyl ethers **3**. The original method for the reductive cleavage of the methyl ethers with metallic sodium gave poor results in our hands because of overreduction of the carbanions **4** to di- and trianions.[19] Replacing the sodium metal by a less than stoichiometric amount of sodium naphthalenide greatly improved the purity of the product hydrocarbons, which were obtained as the *all-E*-isomers by hydrolysis of the sodium salts **4**. DP3 was obtained from phenylacetaldehyde.[20]

Anion Spectra. The cesium salts of the diphenylpolyenes in THF gave UV–vis spectra with concentration-dependent band shapes. The observed effects increase along the series from DP3$^-$Cs$^+$ to DP9$^-$Cs$^+$; Figure 1 (top) shows spectra of DP9$^-$Cs$^+$ at different concentrations as an example. This behavior cannot be due to the formation of higher aggregates, since previous studies

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[•] Abstract published in *Advance ACS Abstracts*, December 15, 1993.

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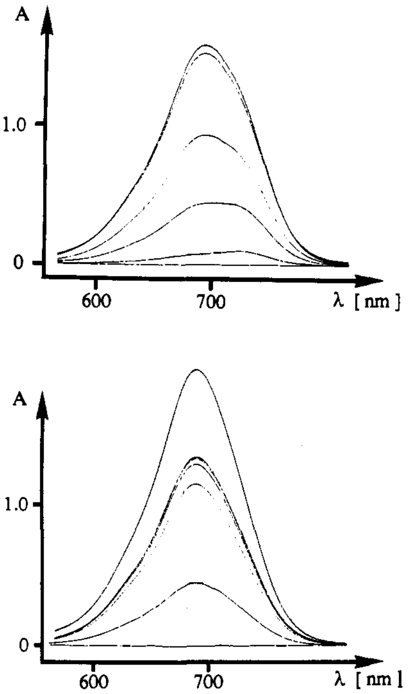

Figure 1. (Top) Concentration dependence of the UV–vis spectrum of DP9$^-$Cs$^+$ in THF showing the equilibrium between ion pairs and free ions. Concentrations range from 10^{-4} to 10^{-5} M in a 1-mm cell. (Bottom) Same as top but THF saturated with CsBPh$_4$ (about 0.1 M).

have found all cesium salts of comparably conjugated hydrocarbon indicators to be monomeric at these concentrations.[21] Instead, dissociation of the cesium ion pairs is occurring into the free ions (eq 1). At lower concentrations, this equilibrium shifts to the

$$R^-Cs^+ \rightleftarrows R^- + Cs^+ \tag{1}$$

side of the free ions and a new band at longer wavelength develops,[22] as shown for DP9$^-$Cs$^+$ in Figure 1 (top).

The simultaneous presence of both ion pairs and free ion would severely complicate the determination of extinction coefficients and p*K*'s for the polyenylcesium ion pairs. However, it was possible to suppress the formation of free polyenyl ions by an increase in the concentration of free cesium ions resulting from addition of cesium tetraphenylborate (CsBPh$_4$). In fact, Figure 1 (bottom) shows that saturating the solutions of DP9$^-$Cs$^+$ in THF with CsBPh$_4$ gives a concentration-independent band shape, indicating a substantial decrease in the amount of free polyenyl anions. The low saturation concentration of $<10^{-3}$ M for CsBPh$_4$ suggests that the added salt does not alter the solvent properties and does not form aggregates with the indicator ion pairs.[23] A control experiment with the much less dissociated cesium salt of 2,3-benzofluorene showed no measurable change in the band shape and extinction coefficient upon the addition of CsBPh$_4$.

In addition to the complications caused by ion pair dissociation, we were also concerned about possible side reactions of the polyenes with the deprotonating agent.[24] For the longer chain polyenes, the base could add to the polyene system in competition with proton abstraction and we would end up with a mixture of two anions with different π-electron systems. If this happened, the band shape of the UV–vis spectrum would depend on the base used for the deprotonation, since different bases should give different ratios of deprotonation and addition. Spectroscopic data for the cesium polyenyls were therefore obtained in THF saturated with CsBPh$_4$, and control experiments were performed with alternative deprotonating agents. Band shapes and extinction coefficients were found to be independent of the base used for deprotonation, and the values listed in Table 1 could be reproduced within ±1 nm for the wavelength and ±2% for the extinction coefficient.

Table 1. Spectra of Diphenylpolyenyl Ion Pairs and Free Ions in THF[a]

compound[b]	Cs,[c] $\lambda_{max}(\epsilon)$	Li, $\lambda_{max}(\epsilon)$	free ions λ_{max}	anions, DMSO,[d] λ_{max}
DP3	538 (57 800)	563 (59 800)	566	558
DP5	572 (117 000)	598 (153 000)	602	591
DP7	621 (144 000)	650 (189 000)	653	642
DP9	672 (161 000)	706 (215 000)[e]	710	696

[a] λ_{max} is given in nm; ϵ is the molar extinction coefficient. [b] Abbreviations are as follows: DP3, 1,3-diphenylpropene; DP5, 1,5-diphenyl-1,3-pentadiene; DP7, 1,7-diphenyl-1,3,5-heptatriene; DP9, 1,9-diphenyl-1,3,5,7-nonatetraene. [c] Determined in THF saturated with cesium tetraphenylborate. [d] Reference 26. [e] In the presence of a 20-fold excess of (triphenylmethyl)lithium, λ_{max} is shifted to 701 nm.

As expected from elementary quantum theory, extending the conjugated chain along the series from DP3 to DP9 leads to a shift of λ_{max} to longer wavelengths and to an increase in the extinction coefficient.[17] The large difference in the λ_{max} between cesium and lithium salts, with the cesium salts absorbing at wavelengths 25–34 nm shorter than the corresponding lithium salts, is consistent with previous observations of different types of ion pairing for the lithium and cesium salts of conjugated carbanions, the cesium salts being always contact ion pairs in THF.[21]

For the determination of thermodynamic constants, the temperature dependence of the polyenylcesium spectra was measured in CsBPh$_4$-saturated THF over the temperature range +25 to −20 °C. The spectrum of DP3$^-$Cs$^+$ underwent a significant change with temperature (Figure 2 (top)), with the shoulder at shorter wavelength decreasing at lower temperatures. On the other hand, the spectra of DP5$^-$Cs$^+$ to DP9$^-$Cs$^+$ showed only the usual narrowing of bandwidth and increase of extinction coefficient at lower temperature, besides a slight shift of λ_{max} to longer wavelengths (Figure 2 (bottom)). These spectra confirm the absence of significant amounts of solvent-separated cesium ion pairs for the diphenylpolyenyls. The equilibrium between SSIP and CIP would not be affected by the added CsBPh$_4$, but is known to shift to the SSIP at lower temperatures.[22] Since a solvent-separated cesium ion pair would have virtually the same λ_{max} as its lithium counterpart, the presence of sizeable amounts of solvent-separated cesium ion pairs should lead to an increase in absorbance at this wavelength in spectra taken at lower temperatures. The example shown in Figure 2 (bottom) demonstrates that this increase does not occur. The fact that no solvent-separated ion pairs were detectable even under conditions where the contact ion pairs dissociate to a considerable extent leads to the conclusion that cesium salts of carbanions generally do not form solvent-separated ion pairs in THF. The electrostatic binding energy of a solvent molecule to the cesium cation is clearly too low to enable the cesium cation to permanently hold a solvation shell of oriented solvent molecules. Conductivity studies of Szwarc et al.[23b] showed this to be the case generally for cesium ions in THF. They found the cesium ion to be unsolvated in THF with a hydrodynamic radius of only 2.3 Å, whereas the sodium ion maintains a stable solvation shell in THF with a hydrodynamic radius of about 3.4 Å. The varying shoulder in the spectra for DP3$^-$Cs$^+$ probably comes from the *E*,*Z*-isomer (vide infra).

Transmetalation Equilibria. Equilibrium constants were determined for the cesium salts and various indicator hydrocarbons

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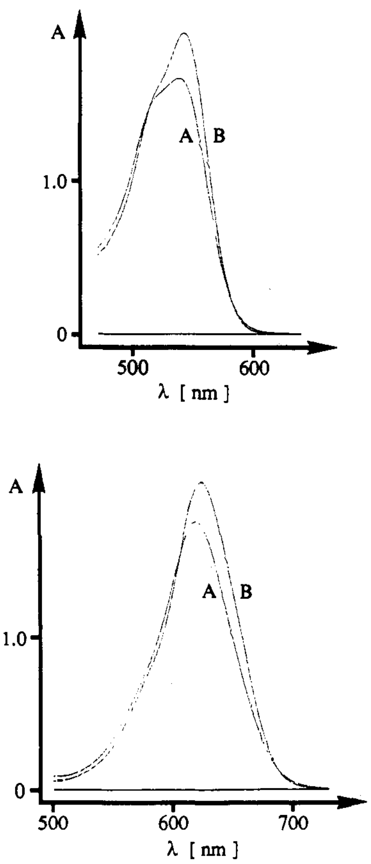


Figure 2. (top) Spectrum of DP3$^-$Cs$^+$ in THF saturated with CsBPh$_4$ at 25 °C (spectrum A) and at -20 °C (spectrum B). (bottom) Same as top for DP7$^-$Cs$^+$.

(eq 2) and were converted to "ion pair pK" values using the pK of fluorene in DMSO (22.90) as the reference.[25]

$$R^-Cs^+ + R'H \rightleftharpoons RH + R'^-CS^+ \qquad (2)$$

For this work the UV-vis spectra of the equilibrium mixtures were deconvoluted by a least-squares fit with the spectra of the individual indicator cesium salts. This improved the precision of the method, particularly in cases where the spectra of the two anions were strongly overlapped. To obtain true cesium ion pair p*K*'s for DP3 to DP9, all measurements involving the diphenylpolyenes were done in THF that was saturated with CsBPh$_4$. A control experiment showed no measurable change in the transmetalation equilibrium between 2,3-benzofluorene and 4,5-methylenephenanthrene upon the addition of CsBPh$_4$; that is, added CsBPh$_4$ has no effect on the ion pair p*K* of the hydrocarbon indicators.

The equilibrium measurements made are summarized in Table 2. At least three measurements were made for each entry. Standard deviations of the resulting Δp*K* values were less than ±0.01 in all but one case. The resulting cesium ion pair p*K* values for the diphenylpolyenes are summarized in Table 3.

Table 2. Transmetalation Equilibria for Cesium Salts in THF at 25 °C

RH[a]	R'H	Δp*K* (±0.01)[b]
Fl	2,3-BF	0.69
4,5-MP	DP9	0.10
4,5-MP	2,3-BF	0.68
4,5-MP	DP7	1.22
DP9	DP7	1.14
2,3-BF	DP7	0.54
2,3-BF	9-*t*-BuFl	0.81
DP7	9-*t*-BuFl	0.26
DP7	DP5	1.49
9-*t*-BuFl	DP5	1.22
9-*t*-BuFI	DP3	3.47[c]
DP5	DP3	2.23
DP3	PDDA	0.26

[a] RH is the more acidic hydrocarbon; abbreviations (p*K*'s)[25] are as follows: Fl, fluorene (22.90); 2,3-BF, 2,3-benzofluorene (19.47); 4,5-MP, 4,5-methylenephenanthrene (22.91); 9-*t*-BuFl, 9-*tert*-butylfluorene (24.39); PDDA, 9-phenyl-10,10-dimethyldihydroanthracene (28.11). See also Table 1. [b] On a per hydrogen basis. [c] ±0.02.

Table 3. p*K* Values for the Diphenylpolyenes in THF at 25 °C[a]

compound	Cs ion pair p*K*	free ion p*K*
DP3	27.85	26.17
DP5	25.62	23.79
DP7	24.14	21.91
DP9	23.01	20.46

[a] p*K* values are on a per hydrogen basis.

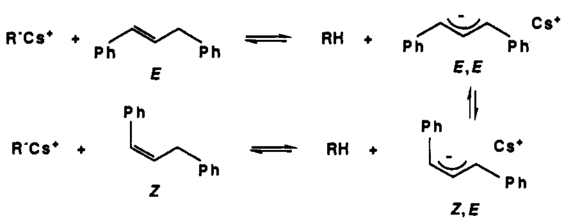
Table 4. Thermodynamic Data for the Equilibria in Eq 2

RH[a]	R'H	Δp*K*[b]	ΔH°, kcal mol^{-1}	ΔS°, eu
DP5	DP3	2.23	-3.59	-1.8
DP7	DP5	1.49	-2.11	-0.3
DP9	DP7	1.14	-1.64	-0.3
2,3-BF	DP7	0.54	-2.81	-13.3[c]

[a] RH is the more acidic hydrocarbon; see Tables 1 and 2 for the key to abbreviations. [b] On a per hydrogen basis. [c] The value after the symmetry component is removed is -14.7 eu.

Thermodynamic data for the transmetalation reactions between the polyenes were determined from p*K* measurements over a temperature range from +25 to -20 °C. The values listed in Table 4 are expected to be correct to about ±0.2 kcal mol^{-1} for $\Delta H°$ and ±0.5 eu for $\Delta S°$. The experiments show only small entropy differences within this series, which means that the p*K* differences among them are predominantly determined by their enthalpy differences. However, the large difference in entropy between the deprotonation of DP7 and the rigid 2,3-benzofluorene suggests that internal rotations in the diphenylpolyene are relatively frozen in the carbanion.[21]

Stereoisomer Equilibria. Detailed investigations of DP3$^-$Li$^+$ in THF have shown it to exist as a mixture of the *E,E*- and *E,Z*-isomers, which equilibrate rapidly at room temperature.[12-14,16] Protonation of this mixture leads to both the *E*- and *Z*-isomer of DP3. As shown in eq 3, the same process in the cesium ion pair



(3)

proton transfers would catalyze the equilibrium between stereoisomers and tautomers of DP3 to DP9.

The direct experimental acidity values are those for an equilibrium set of hydrocarbon isomers equilibrating with an equilibrium mixture of carbanion conformers. For a more detailed analysis of the acidity data, we sought to determine the position of these equilibria under conditions close to those used for the p*K* determinations, by taking ^{1}H NMR spectra in THF-d_8 at room temperature with (diphenylmethyl)cesium as the base.

The hydrocarbon equilibrations were analyzed in the presence of catalytic amounts of the polyenylcesium by integrating the signals of the hydrocarbon methylene protons. For DP3 and DP5 the structures of all isomers could be determined from the spin coupling constants. For the minor isomers of DP7 and DP9

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Table 5. Equilibria among Diphenylpolyene Stereoisomers in THF[a]

compound	configuration[b]	fraction, %
DP3	*E*	>99
	Z	<1
DP5	*E,E*	86
	E,Z	12
	others[c]	<2
DP7	*E,E,E*	80
	E,E,Z	11
	E,Z,E	8
	others[c]	1
DP9	*E,E,E,E*	68
	E,E,E,Z	11
	E,E,Z,E	10
	E,Z,E,E	10
	others[c]	<1

[a] Determined at 22 °C by ^{1}H NMR spectroscopy, integrating the CH_2 signals; equilibria were established via the cesium salts. [b] Assignments for DP7 and DP9 are by analogy. [c] Including positional isomers of the double bonds.

Table 6. Equilibria among (Diphenylpolyenyl)cesium Stereoisomers in THF[a]

compound	configuration	fraction, %
DP3$^-$Cs$^+$	*E,E*	85
	E,Z	15
DP5$^-$Cs$^+$	*all-E*	74–93
	others	7–26
DP7$^-$Cs$^+$	*all-E*	70–94
	others	6–30

[a] Determined at 22 °C by ^{1}H NMR spectroscopy.

tentative structural assignments were made on the basis of the multiplicity and chemical shifts of their methylene proton signals. The results, summarized in Table 5, show that the polyene systems tend to retain maximum conjugation, with isomers that contain the methylene group between two double bonds accounting for less than 2% of the isomer mixtures in all cases. However, the energy differences are much smaller between stereoisomers at double bonds not neighboring the phenyl group and the amount of *Z*-isomers in the equilibrium increases steadily with increasing chain length from less than 2% for DP3 to about 30% for DP9.

The analysis of anion stereochemistry gave less conclusive results. Spectra had to be recorded with an excess of (diphenylmethyl)cesium, and therefore only protons bonded to charge-carrying carbon atoms of the chain could be observed, while the other signals were hidden under the phenyl resonances. In addition, the linewidths of the diphenylpolyenyl signals increased dramatically on going from DP3$^-$Cs$^+$ to DP9$^-$Cs$^+$ with the signals of DP9$^-$Cs$^+$ becoming too broad for integration. Variation of the temperature over a 30 °C range gave little change in the linewidths, which suggests the presence of a radical species such as the diphenylpolyenyl radical or radical dianion in small amounts, rapidly exchanging an electron with the diphenylpolyenyl ion. Although incomplete, the spectra show the major isomers of DP3$^-$Cs$^+$, DP5$^-$Cs$^+$, and DP7$^-$Cs$^+$ to have the *all-E*-configuration.[13] Tolbert and Ogle report[3a] that the higher DP anions in DMSO exist only in the fully extended *all-E*-conformation. In the spectrum of DP3$^-$Cs$^+$, 15% of the *Z*-isomer could be detected, an amount significantly greater than has been reported for DP3$^-$Li$^+$.[9-13] The only signals in the spectra of DP5$^-$Cs$^+$ and DP7$^-$Cs$^+$ that could not be ascribed to the base or to the *all-E*-isomer are one doublet in each spectrum. The isomer ratios given in Table 6 were therefore derived on the assumption that for both spectra this signal represents one proton of a *Z*-isomer. The lower limit for the amount of *Z*-isomers is obtained assuming that only one *Z*-isomer is present, of which one proton signal is observed, and that the other signals of this isomer are not hidden under the signal of the *all-E*-isomer. The upper limit is based on the assumption that all possible isomers with one *Z*-configured bond (two for DP5$^-$Cs$^+$ and three for DP5$^-$Cs$^+$) are present in equal amounts, but only the signal for one proton of one of these isomers is observed whereas all other signals of the *Z*-isomers are hidden under the signals of the *all-E*-isomer.

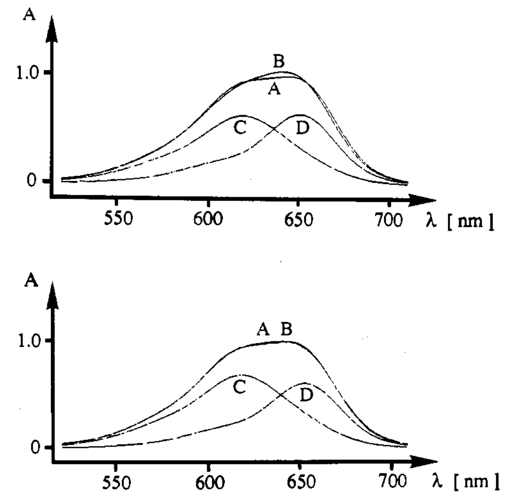

Figure 3. (top) Spectral fit for a spectrum of DP7$^-$Cs$^+$ in THF (spectrum A) with the spectrum of DP7$^-$Cs$^+$ in THF saturated with $CsBPh_4$ (spectrum C) and the spectrum of DP7$^-$Li$^+$ in THF (spectrum D). Spectrum B is the sum of spectra C and D. (bottom) Same as top but spectrum D is offset to longer wavelengths by 3.2 nm.

Because both the hydrocarbon and its conjugate base are mostly in the *all-E*-configuration, the experimental p*K* values do not differ much from the values involving only the *all-E*-configurations.

Dissociation Constants. The contribution of free ions to the UV–vis spectra of the cesium diphenylpolyenyls in THF complicates the measurement of the ion pair p*K*'s, but it also opens the way to spectroscopic determination of the dissociation constants K_d for the cesium diphenylpolyenyl ion pairs. If we assume that in THF any cesium hydroxide present is essentially not dissociated and that the dissociation of the cesium diphenylpolyenyl ion pairs is the only source of free cesium ions, we can substitute their concentration with the concentration of the free diphenylpolyenyl ions

$$R^-Cs^+ \rightleftarrows R^- + Cs^+ \tag{4}$$

$$K_d = \frac{[R^-][Cs^+]}{[R^-Cs^+]} = \frac{[R^-]^2}{[R^-Cs^+]} = \frac{c_{FI}^{\,2}}{c_{IP}} \tag{5}$$

where c_{FI} is the concentration of free ions and c_{IP} is the concentration of ion pairs. Therefore, all we need to determine K_d are the concentrations of the free and ion paired diphenylpolyenyl ions. They were obtained by deconvoluting the UV–vis spectra of the cesium diphenylpolyenyls in neat THF with the spectra of the free diphenylpolyenyl ions and their cesium ion pairs. This simple approach is possible, of course, only when the ion pairs are of a given type; in the present system, the cesium ion pairs are all CIP. The spectra of the cesium ion pairs were directly available from the measurements in $CsBPh_4$-saturated THF. However, the spectra of the free diphenylpolyenyl anions in THF could not be determined directly. Instead, they were modeled by the spectra of their lithium salts. The free ions and solvent-separated lithium ion pairs are expected to have virtually identical extinction coefficients, but the λ_{max} of the lithium ion pairs should be shifted to slightly shorter wavelengths with respect to the free ions.[22] In fact, Figure 3 demonstrates that the spectral fits of the cesium diphenylpolyenyl spectra in neat THF with the cesium ion pair spectra and the lithium diphenylpolyenyl spectra improve substantially if the lithium salt spectrum is offset to longer wavelengths by 3–4 nm. UV–vis spectra of the cesium

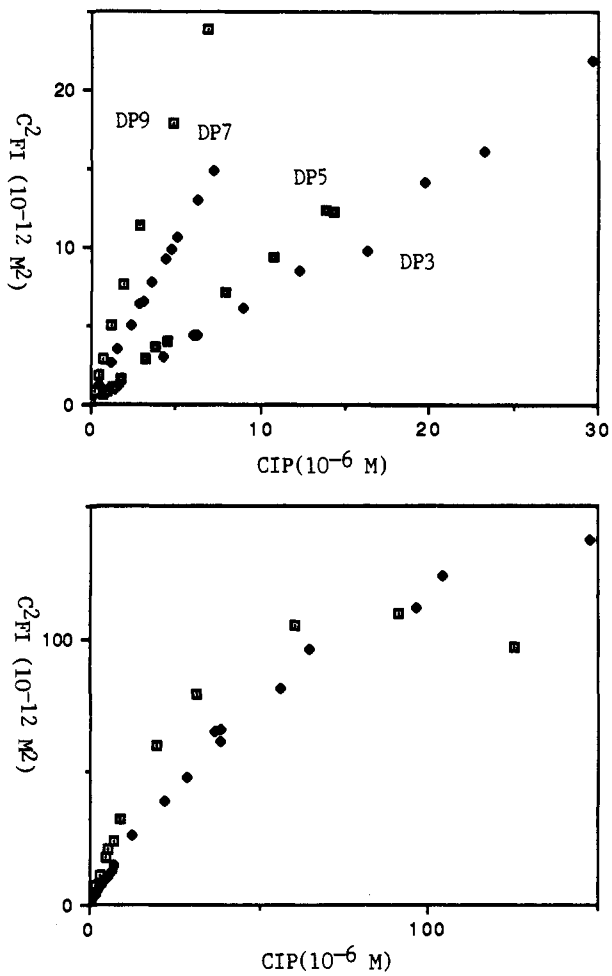

Figure 4. Plots of c_{FI}^2 versus c_{IP} for the concentrations of free ions and ion pairs obtained by deconvoluting the UV–vis spectra of the cesium diphenylpolyenyls in THF. (top) Data obtained at a 0.1-cm pathlength. (bottom) Data obtained at a 1-cm pathlength.

diphenylpolyenyls recorded over a 10–100-fold concentration range were deconvoluted with this method with consistently less than 5% deviation between the experimental and modeled spectra. The corrected values for the free ion λ_{max} are included in Table 1. The free ion spectra have also been reported by Tolbert and Ogle[26] for DMSO solutions; their values for λ_{max} are also included in Table 1 and are at slightly shorter wavelengths than the THF values.

From the spectral measurements in THF, the equilibrium concentrations of free ions (c_{FI}) and ion pairs (c_{IP}) were calculated with the extinction coefficients from Table 1. Plots of c_{FI}^2 versus c_{IP} (Figure 4) show the expected linear correlation at low concentrations. However, at higher total concentrations, the free ion concentrations determined this way seem to be too low and the errors appear to increase with increasing K_d. The most likely reason for this behavior is the presence of small amounts of free ions in the spectra of the cesium ion pairs. For DP7⁻Cs⁺ and DP9⁻Cs⁺ the dissociation constants appear to be larger than for $CsBPh_4$[23] and the addition of $CsBPh_4$ cannot completely suppress the ion pair dissociation. If the spectra of the ion pairs contain some contribution of the free ions, the fraction of the free ions erroneously assigned to the contact ion pair by the deconvolution will increase as the ratio of contact ion pairs to free ions grows with increasing total concentration. However, the data can be corrected for the presence of free ions in the ion pair spectra in a straightforward way; linear plots were obtained for c_{FI}^2 versus c_{IP} by assuming free ion fractions of 2% (DP5⁻Cs⁺), 5% (DP7⁻Cs⁺), and 13% (DP9⁻Cs⁺) in the ion pair spectra (Figure 5). Dissociation constants were derived from the slopes of these plots and are listed in Table 7. These numbers are probably accurate to ±20%, although the precision within the series of the (diphenylpolyenyl)cesiums is probably somewhat better.

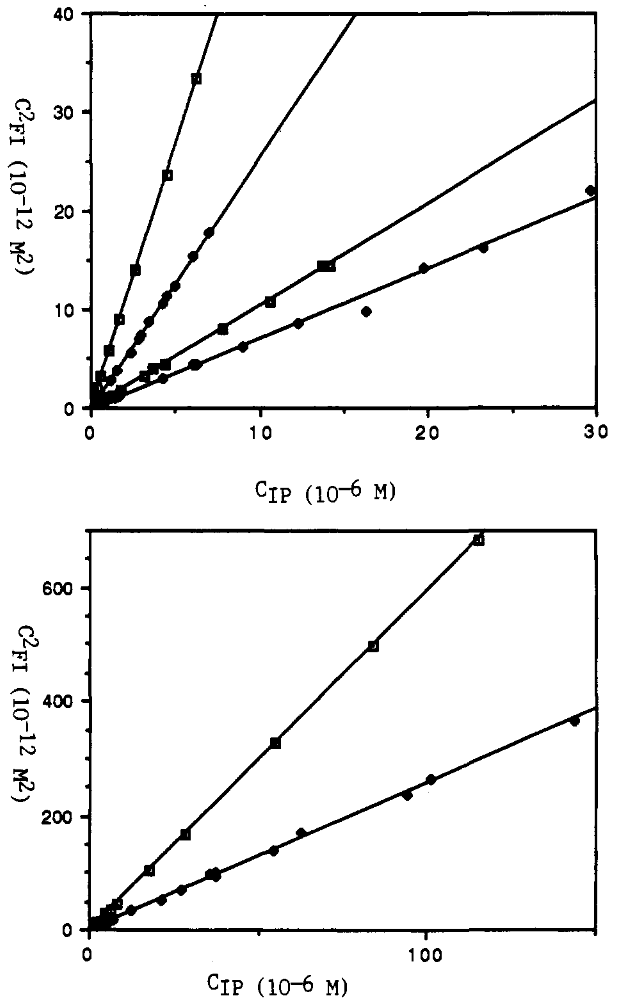

Figure 5. Same as Figure 4 but data corrected for the presence of free ions in the spectra of the cesium diphenylpolyenyls in THF saturated with $CsBPh_4$.

Table 7. Dissociation Constants of (Diphenylpolyenyl)cesium in THF at 25

compound	10^6K_d, M
DP3⁻Cs⁺	0.7
DP5⁻Cs⁺	1.0
DP7⁻Cs⁺	2.5
DP9⁻Cs⁺	5.3

The dissociation constants in Table 7 are 1–2 orders of magnitude higher than those of cesium salts of fluorenyl-type hydrocarbons.[27] The extended conjugation of the polyenyl anions results in reduced electrostatic interaction with the cesium cation and permits greater dissociation. By comparison, Burley and Young[7a] reported that conductivity studies indicate about 1% dissociation in 10^{-4} M solutions of a lithium diphenylallyl compound; the corresponding $K_d = 10^{-4}$ M, an order of magnitude higher than that of SSIP lithium fluorenyls.[26]

The variations in the dissociation constants of cesium salts can be rationalized using a simple electrostatic model.[27,28] The charge distribution from π-SCF calculations performed on force field optimized geometries of the carbanions gives point fractional

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[27] Kaufman, M. J.; Gronert, S.; Streitwieser, A. *J. Am. Chem. Soc.* **1988**, *110*, 2829.

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Table 8. Calculated Cation Affinities of Diphenylpolyenyl Anions[a]

compound	cation affinity, kcal mol^{-1}
$DP3^-$	77.0
$DP5^-$	72.8
$DP7^-$	69.2
$DP9^-$	66.4

[a] Calculated with π-charges from a π-SCF calculation for an interionic distance of 3.1 Å (see refs 27–29).

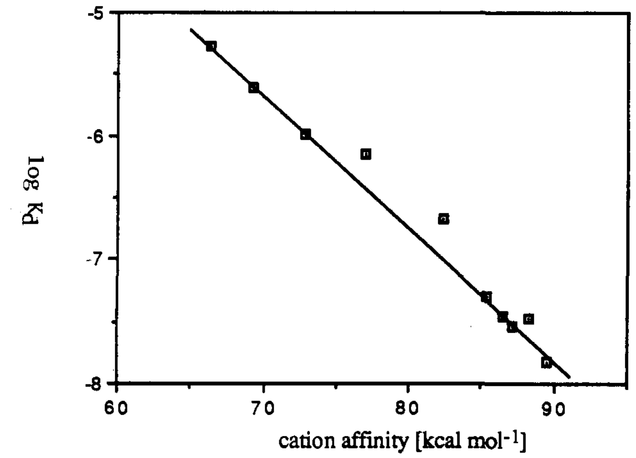

Figure 6. Plot of log K_d versus calculated cation affinities for cesium salts of conjugated hydrocarbons. The results of this work (Table 8) are combined with values from ref 27.

charges that were used to determine the total electrostatic energy of a fixed positive charge located at the electrostatic minimum and 3.1 Å from the carbanion.[29] The resulting cation affinities are summarized in Table 8. Figure 6 combines these values with those obtained in a similar manner for other π-carbanions (fluorenyl, benzofluorenyl, etc.) and compares the calculated cation affinities to the experimental dissociation contants of cesium salts.[27] The figure shows a remarkably good correlation over the entire 300-fold range of K_d despite the simplifying assumptions used. Other definitions of the charge distribution would probably not change this qualitative result.

The slope of the correlation shown in Figure 6, 1/6.6, compares well with the dielectric constant of tetrahydrofuran, 7.6. The fact that the dissociation process can be rationalized so well by a model that treats the solvent as a continuous dielectric is further evidence for the absence of any specific ion–solvent interactions for the cesium salts of hydrocarbon indicators in THF.

The dissociation constants in Table 7 can be combined with an earlier determined dissociation constant for cesium fluorenide to calculate the free ion p*K*'s of the diphenylpolyenes in THF.[27] Table 3 includes these results that are also referenced to the DMSO p*K* of fluorene, 22.90 (per hydrogen). From the results of earlier comparisons, these free ion p*K* values are probably quite close to the corresponding values in DMSO. The free ion p*K*'s of the diphenylpolyenes are lower than their cesium ion p*K*'s because their cesium salts are more dissociated in THF than is the reference system of fluorenylcesium. They are also spread over a wider p*K* range because of the change in K_d along this series.

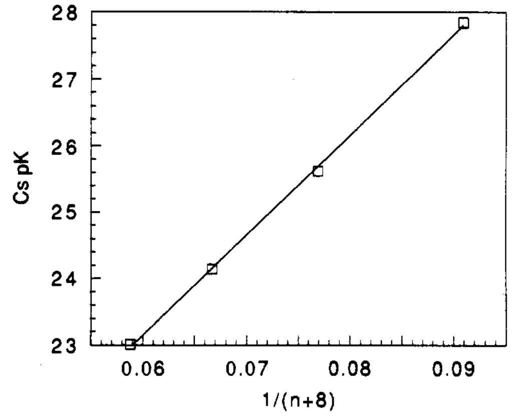

Figure 7. Plot of Cs ion pair p*K*'s of DP*n* vs $(n + 8)^{-1}$. The line shown is $pK = 14.10 + 150.7(n + 8)^{-1}$, $r = 0.9996$.

Delocalization Energies. The lower p*K* values of diphenylpolyenes with increasing chain length undoubtedly result from increasing delocalization of charge. Because of the monotonic dependence of p*K* on the chainlength, *n*, anything that is also monotonic in *n* could give a more or less acceptable correlation but perhaps without physical significance. One especially interesting correlation is that with $(n + 8)^{-1}$, which was shown by Tolbert and Ogle[3] to be particularly effective in their important studies of charge distributions in the diphenylpolyenyl anions. Their method is an application of simple electron-in-a-box theory in which the box is extended by four units on each side to account for the phenyls. This type of approach has been applied generally to one-electron properties such as orbital energies[30] and does not generally apply to total energies and energy differences; however, correlations between one-electron properties and total energy functions are common in HMO theory for alternant hydrocarbons and ions.[31] In the event, the p*K*'s give an excellent correlation with $(n + 8)^{-1}$ as shown in Figure 7. This interesting and useful if *empirical* correlation permits extrapolation to the hypothetical ion pair p*K* of the infinite chain of about 14. The choice of four for the contribution of each phenyl is only approximate. Any choice of comparable magnitude will give a correlation virtually as good but will extrapolate to a somewhat different infinity value.

Another significant relation is with the relative π-energies or delocalization (resonance) energies. The availability of the relative free ion acidities for the diphenylpolyenes allows direct comparisons with calculated π-electron energies. Free ion acidities for highly conjugated carbanions are independent of solvent for aprotic solvents as different in polarity as THF and DMSO.[27] Furthermore, Bordwell and Taft found proton-transfer reactions between pairs of highly conjugated hydrocarbons and their anions to have the same $\Delta G°_r$ in the gas phase and in DMSO solution.[32] On this basis we can use the differences in free ion acidities among the diphenylpolyenes to obtain the intrinsic resonance stabilization of the diphenylpolyenyl anions largely unbiased by solvation effects.

Some assumptions, however, are needed to get experimental differences in resonance energy that can be directly compared with calculations. The free ion p*K* values in Table 3 are converted to $\Delta G°$ values in Table 9. We use $\Delta G°$ values rather than $\Delta H°$ because for reactions in solution relative rates and equilibrium constants are frequently more fundamental than enthalpy values.[33]

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(29) Calculations were performed for all potential cation coordination sites next to and between charge-carrying carbon atoms of the chain. The partial π-charges of the anion were treated as point charges within the plane of the carbon nuclei, and the cation was modeled by a positive point charge at a distance of 3.1 Å to this plane. For all diphenylpolyenides, the symmetrical position over the middle of the chain was found to be the preferred cation coordination site and the values given in Table 8 were obtained with this ion pair geometry.

(30) Applications of "free electron" theory were common in the days before computers. For early reviews, see: Bayliss, N. S. *Q. Rev., Chem. Soc.* **1952**, *6*, 319. Kuhn, H. *Experientia* **1953**, *9*, 41. For spectral correlations of the present type, see refs 17 and 26. A recent application to poly-π-systems is given: Bredas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *015*, 6555.

(31) Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; John Wiley and Sons, Inc.: New York, 1961. Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975.

(32) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463.

(33) This point has been made frequently in the literature. For one discussion, see: Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; John Wiley and Sons, Inc.: New York, 1961; p 311.

Table 9. Energy Differences for Deprotonation Compared to Theoretical Differences[a]

compound	ΔG° [b] ionic acidity	ΔG°_{corr} *Z*-isomers	ΔG°_{corr} anion *Z*-isomers	$-\Delta\Delta H^\circ$ *all-E* acidity
DP3	35.71	0	0.10	0
DP5	32.46	–0.09	0.04–0.18	3.3–3.4
DP7	29.89	–0.13	0.04–0.21	5.8–6.0
DP9	27.91	–0.23	0.04–0.21	7.9–8.1

[a] All values in kcal mol^{-1}. [b] From ionic pK values in Table 3.

Table 10. π-Electron Energies from PIMM91[a]

compound	hydrocarbon E_π, eV	anion E_π, eV	ΔE_π (rel to DP3), kcal mol^{-1}
DP3	-17.010	-21.463	102.5 (0)
DP5	-19.244	-23.930	107.9 (5.4)
DP7	-21.508	-26.305	110.5 (8.0)
DP9	-23.765	-28.650	112.5 (10.0)

[a] Reference 35.

The ΔS° values, in any event, change by only small amounts in the ion pair equilibria of this series (Table 4). The ion pair dissociation of cesium contact ion pairs in THF is expected to show a large ΔS°_d. Szwarc et al. have determined the temperature dependence of the dissociation constant of $CsBPh_4$,[23] and van't Hoff plot of their data gives $\Delta S^\circ_d > 30$ eu. However, the close correlation between the dissociation constants and the electrostatic energies of the ion pairs as demonstrated by Figure 6 suggests that ΔS°_d is virtually the same for all of these cesium ion pairs in THF because of the absence of specific ion solvent interactions. Thus, the effects of ΔS°_d may be expected to approximately cancel those of the proton-transfer reactions between the diphenylpolyenes and their anions.

The ΔG° values must also be corrected for the effects of stereoisomer equilibration to get the ΔG° values for the equilibria between the *all-E*-diphenylpolyenes and the free *all-E*-diphenylpolyenyl anions. In these corrections, we must also neglect any variation in ΔS° values of the stereoisomer equilibria because they cannot be determined with sufficient precision by our experimental techniques. Compared with ΔS°_d, the entropy differences between the stereoisomers of the diphenylpolyenes and their anions are expected to be small because of the small structural differences among the stereoisomers. In fact, the data reported by Boche et al.[13] for the equilibrium between the *E,E*- and *E,Z*-isomers of $DP3^-Li^+$ give a van't Hoff plot with $\Delta S^\circ <$ 1 eu. We therefore assume $\Delta S^\circ = 0$ for all of these stereoisomer equilibria with probably little error.

With these assumptions for the entropies of the dissociation and isomerization reactions, we derive eq 6 for the corrections

$$\Delta\Delta H^\circ = \Delta\Delta G^\circ = -\frac{1}{RT}\ln\frac{K_{corr}}{K_{exp}} \qquad (6)$$

that have to be made to the enthalpy differences of Table 4. The individual correction terms are listed in Table 9 together with the net differences in acidity listed as a range of $\Delta\Delta H^\circ$ values relative to DP3; that is, the value for DP3 is set to 0 kcal mol^{-1}. The corrections for the stereoisomerization of the anions are given for both the lower and upper limits of *Z*-isomers, and the uncertainty in the correction terms turns out to be rather small despite the large uncertainty in the NMR experiments. Since the correction terms are small, we simply estimate the unknown amount of *Z*-stereoisomers for DP9 to be the same as for DP7.

Since their introduction almost 25 years ago,[4] Dewar-type resonance energies (RE) have become a widely accepted tool for the description and classification of conjugated hydrocarbons. They can be easily determined from the experimental heats of formation and a set of thermochemical increments for the hypothetical nondelocalized reference state. Dewar and De Llano have shown that these resonance energies can be calculated with reasonable precision for planar, nonstrained hydrocarbons using π-SCF methods.[34] For charged systems, however, no absolute values for RE can be determined because the reference state for RE is only defined for neutral hydrocarbons. Nonetheless, it is possible to determine differences ΔRE between carbanions.

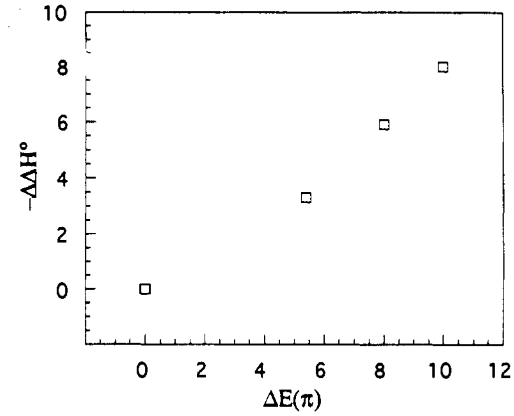

Figure 8. Plot of experimental differences $-\Delta\Delta H^\circ_{acid}$ in energy of deprotonation versus calculated π-electron energy differences ΔE_π between the anion and hydrocarbon (from π-SCF calculations) for the diphenylpolyenes.

Table 11. AM1 and PIMM91 Energies (kcal mol^{-1}) for DP*n* Hydrocarbons and Anions

	AM1			PIMM91		
DP*n*	RH	R^-	ΔE(rel)	RH	R^-	ΔE(rel)
3	55.29	33.02	0	51.7	–20.7	0
5	68.30	41.59	4.44	64.9	–11.4	3.8
7	81.20	51.37	7.56	77.7	–1.5	6.7
9	94.08	61.94	9.87	90.6	9.3	8.8

The corrected energy differences of Table 9 are then an experimental measure for the differences between the Dewar-type resonance energies of the diphenylpolyenyl anions and can be used to test the validity of theoretical calculations for the anion resonance energy. They are best compared with the calculated differences ΔE_π between the π-electron eneries of the anion and hydrocarbon. Since all diphenylpolyene hydrocarbons have almost the same resonance energy, ΔE_π and the anion resonance energy will differ by an essentially constant factor. Figure 8 shows a plot of the experimental corrected acidity differences ΔH° versus ΔE_π values calculated with π-SCF values for the force field optimized geometries of the diphenylpolyenes and diphenylpolyenyls determined with the PIMM91 program.[35] The correlation is monotonic but not linear.

Alternatively, the experimental data can be compared with all-valence electron semiempirical calculations, and we report here such a comparison with Dewar's AM1 method[36] using Mopac 6.1 as implemented in the CAChe system.[37] AM1 has been shown to give satisfactory deprotonation enthalpies for a number of compounds.[38] In the present application, the differences among closely related compounds are undoubtedly more reliable than the absolute values. Some results are summarized in Table 11.[39] the DP*n* (*n* = 3 to 9) hydrocarbons all had comparable minimized structures with alternating single (1.44–1.45 Å) and double bonds (1.34–1.35 Å) along the chain, a HCH bond angle of 107°, and the plane of benzylic benzene ring 69° relative to the plane of the conjugated system. The energies vary essentially linearly with

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(37) CAChe Scientific Inc., Beaverton, OR.

(38) Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 8075.

(39) Additional details are available from the senior author.

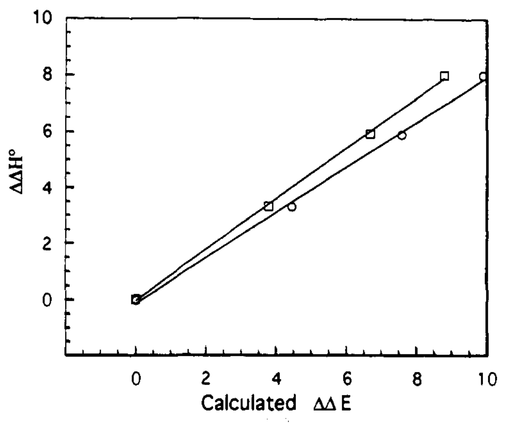

Figure 9. Plots of $-\Delta\Delta H°$ acidity values from Table 11 with AM1 energy differences (circles) and PIMM91 calculations (squares) from Table 11. The linear correlations are given by $\Delta\Delta H° = -0.115 + 0.807\Delta\Delta E$(AM1) ($R = 0.999$); $\Delta\Delta H° = -0.064 + 0.905\Delta\Delta E$(PIMM) ($R = 0.9996$).

the chain length, $\Delta H_f° = 35.94 + 6.464n$. The minimized structures of the *trans* anions are planar with 1.36–1.41-Å CC bond lengths along the chain. The CCC bond angles along the chain are 122–125°, somewhat greater than ideal sp^2. The $\Delta H_f°$ values of the carbanions are not linear in n. The values from $n = 3$ to 11 fit a third-order polynomial, $\Delta H_f° = -22.98 - 2.681n - 0.2404n^2 + 0.00635n^3$. The requirement for higher order terms is indicative of charge delocalization. A comparison of $\Delta\Delta H_f° = \Delta H_f°(R^-) - \Delta H_f°(RH)$ with the corrected acidity values $\Delta\Delta G°$ given in Table 9 is shown in Figure 9. The correlation is excellent, and the slope of 0.8 is not far from unity. Some decrease is expected from the comparison of a gas-phase calculation with solution equilibria.

The experimental data were also compared with molecular mechanics calculations as given by PIMM91. Results are summarized in Table 11 and in Figure 9. The heats of formation of the hydrocarbons are uniformly about 3.5 kcal mol^{-1} lower than those given by AM1; those for the anion are far too negative, undoubtedly because no account is taken of the electronic effects of the negative charge. Differences in ΔE values for the series, however, give a remarkably good correlation with the experimental differences. Indeed, the correlation is even better than that with AM1. Finally, we close with the amusing result that the correlation of $\Delta\Delta G°$ with $(n + 8)^{-1}$ is every bit as good as that with AM1 or PIMM91; $-\Delta\Delta G° = 22.75 - 250.94/(n + 8)$, $r = 0.9998$!

Experimental Section

General. Starting materials for syntheses were obtained from commercial sources and used without further purification. Cesium tetraphenylborate was prepared by a literature procedure.[40] Melting points were determined on a Buchi melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on either a Bruker AM 500 spectrometer or the UCB-200 (a superconducting 200-MHz instrument); chemical shifts are given in ppm downfield from tetramethylsilane. GC-MS was performed with a HP 5890A gas chromatograph equipped with a HP 5970 mass sensitive detector on DB-5 and DB-WAX capillary columns (30 m, 0.25 μm). UV–vis spectra were recorded on an IBM 9430 spectrometer. HPLC was performed with a Waters 501/484/810 system on a μ-Bondapac-C18 column using a water/acetonitrile gradient and UV detection.

Carbon Acids. Most hydrocarbon indicators were available from previous studies. (*E*)-1,3-Diphenylpropene was prepared by a literature procedure;[20] DP5, DP7, and DP9 were synthesized by the general procedure outlined below for DP9. Purities were assessed by GC-MS and HPLC to be at least 99.9% for DP3 and DP7, 99.7% for DP5, and 95% for DP9.

(*E,E,E,E*)-1,9-Diphenyl-1,3,6,8-nonatetraen-5-one. In 1 l two-necked, round-bottom flasks equipped with a mechanical stirrer, 25.2 g (0.625 mol) of NaOH was dissolved in 250 mL of water and 200 mL of ethanol and cooled to 20 °C. A mixture of 33.0 g (0.25 mol) of *trans*-cinnamaldehyde and 7.25 g (0.125 mol) of acetone was added in two portions to the well-stirred mixture, with 15 min between the additions. Stirring was continued for 30 min, and the precipitated product was collected on a Buchner funnel, washed with water, and dried in vacuo over calcium chloride. Recrystallization from ethanol gave 25.05 g (70%) of yellow needles, mp 139–141 °C (lit.[41] mp 144 °C).

(*E,E,E*)-1,7-Diphenyl-1,3,6-heptatrien-5-one was prepared by the same procedure from *trans*-cinnamaldehyde and benzalacetone, yellow crystals from ethyl acetate: mp 110–111 °C (lit.[42] mp 110–111 °C).

(*E,E,E,E*)-1,9-Diphenyl-1,3,6,8-nonatetraen-5-ol. (*E,E,E,E*)-1,9-Diphenyl-1,3,6,8-nonatetraen-5-one (14.36 g, 50.1 mmol) was suspended in 200 mL of methanol and cooled to 0 °C, and 3.82 g of $NaBH_4$ (101 mmol) was added. Sodium methoxide was added in small portions to the stirred reaction until the evolution of hydrogen ceased, and stirring was continued for 5 h until all the starting material was consumed (TLC). The mixture was diluted with 500 mL of water and extracted with ether. The extract was washed with water and dried with $MgSO_4$, and the ether was removed by rotary evaporation. Recrystallization of the residue from hexane/toluene gave 12.2 g (85%) of a pale yellow solid: mp 97–100 °C (lit.[43] mp 103–105 °C); ^{1}H NMR ($CDCl_3$) δ 7.2–7.5 (m, 10 H), 6.79 (dd, J = 15.5, 10.3 Hz, 2 H, H(2,8)), 6.57 (d, J = 15.5 Hz, 2 H, H(1,9)), 6.44 (ddd, J = 15.1, 10.3, 1.0 Hz, 2 H, H(3,7)), 5.86 (dd, J = 15.1, 6.6 Hz, 1 H, H(5)), 1.85 (s, 1 H).

Prepared by the same procedure: (*E,E*)-1,5-Diphenyl-2,4-pentadien-1-ol from (*E,E*)-1,5-diphenyl-2,4-pentadien-1-one, colorless crystals from cyclohexane: mp 85 °C (lit.[43] mp 79 °C); ^{1}H NMR ($CDCl_3$) δ 7.2–7.4 (m, 10 H), 6.77 (dd, J = 15.5, 10.2 Hz, 1 H, H(2)), 6.56 (d, J = 15.8 Hz, 1 H, H(1)), 6.46 (ddd, J = 14.9, 10.6, 1.1 Hz, 1 H, H(3)), 5.98 (dd, J = 15.0, 6.5 Hz, 1 H, H(4)), 2.10 (s, 1 H).

(*E,E*)-1,5-Diphenyl-1,4-pentadien-3-ol from (*E,E*)-1,5-diphenyl-1,4-pentadien-3-one, colorless crystals from cyclohexane: mp 72 °C (lit.[43] mp 64–65 °C); ^{1}H NMR ($CDCl_3$) 7.2–7.4 (m, 10 H), 6.67 (dd, J = 15.9, 0.7 Hz, 2 H, H(1,5)), 6.31 (dd, J = 15.9, 6.4 Hz, 2 H, H(2,4)), 4.99 (t, J = 6.2 Hz, 1 H, H(3)), 1.91 (s, 1 H).

(*E,E,E*)-1,7-Diphenyl-1,4,6-heptatrien-3-ol from (*E,E,E*)-1,7-diphenyl-1,4,6-heptatrien-3-one, colorless crystals from hexane/benzene: mp 89 °C (lit.[43] mp 81 °C); ^{1}H NMR ($CDCl_3$) 7.2–7.4 (m, 10 H), 6.79 (dd, J = 15.6, 10.5 Hz, 1 H, H(2)), 6.63 (d, J = 15.9 Hz, 1 H, H(7)), 6.58 (d, J = 15.7 Hz, 1 H, H(1)), 6.47 (dd, J = 15.2, 10.6 Hz, 1 H, H(3)), 6.27 (dd, J = 15.9, 6.5 Hz, 1 H, H(6)), 5.91 (dd, J = 15.2, 6.5 Hz, 1 H, H(4)), 4.91 (t, J = 6.2 Hz, 1 H, H(5)), 1.87 (s, 1 H).

(*E,E,E,E*)-1,9-Diphenyl-9-methoxy-1,3,5,7-nonatetraene. A solution of 8.81 g (30.5 mmol) of (*E,E,E,E*)-1,9-diphenyl-1,3,6,8-nonatetraen-5-ol in 200 mL of methanol was cooled to 0 °C, and 0.5 mL of 10% H_2SO_4 in methanol was added. After being stirred for 1 h at 0 °C, the mixture was neutralized with triethylamine and cooled to −70 °C. The precipitate was collected on a Buchner funnel and dried to give 8.41 g (91%) of bright yellow crystals: mp 57–59 °C; ^{1}H NMR ($CDCl_3$) 7.15–7.40 (m, 10 H), 6.82 (dd, J = 15.6, 10.0 Hz, 1 H, H(2)), 6.55 (d, J = 15.6 Hz, 1 H, H(1)), 6.25–6.43 (m, 5 H), 5.81 (dd, J = 15.0, 7.1 Hz, 1 H, H(8)), 4.69 (d, J = 7.2 Hz, 1 H, H(9)), 3.33 (s, 3 H).

Prepared by the same procedure: (*E,E*)-1,5-Diphenyl-5-methoxy-1,3-pentadiene from (*E,E*)-1,5-diphenyl-2,4-pentadien-1-ol or from (*E,E*)-1,5-diphenyl-1,4-pentadien-3-ol, colorless liquid: ^{1}H NMR ($CDCl_3$) 7.2–7.4 (m, 10 H), 6.77 (dd, J = 15.6, 10.2 Hz, 1 H, H(2)), 6.54 (d, J = 15.6 Hz, 1 H, H(1)), 6.41 (ddd, J = 15.1, 10.2, 0.9 Hz, 1 H, H(3)), 5.89 (dd, J = 15.1, 7.0 Hz, 1 H, H(4)), 4.72 (dd, J = 7.0, 0.7 Hz, 1 H, H(5)), 3.34 (s, 3 H).

(*E,E,E*)-1,7-Diphenyl-7-methoxy-1,3,5-heptatriene from (*E,E,E*)-1,7-diphenyl-1,4,6-heptatrien-3-ol, colorless crystals: mp 44 °C; ^{1}H NMR ($CDCl_3$) 7.18–7.39 (m, 10 H), 6.80 (dd, J = 15.6, 10.1 Hz, 1 H, H(2)), 6.55 (d, J = 15.6 Hz, 1 H, H(1)), 6.30–6.42 (m, 3 H), 5.82 (dd, J = 14.1, 7.0 Hz, 1 H, H(6)), 4.70 (d, J = 7.0 Hz, 1 H, H(7)), 3.34 (s, 3 H).

(*E,E,E,E*)-1,9-Diphenyl-1,3,5,7-nonatetraene (DP9). (E,E,E,E)-1,9-Diphenyl-9-methoxy-1,3,5,7-nonatetraene (8.41 g, 27.8 mmol) was dissolved under argon in 70 mL of THF and cooled to −70 °C. A freshly prepared solution of 0.57 M sodium naphthalenide (80 mL, 45.6 mmol) in THF was slowly added over a period of 1 h, and the mixture was stirred for another 15 min at −70 °C. After the addition of 10 mL of methanol, the mixture was warmed to room temperature, poured into brine, and

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extracted with ether. The extract was repeatedly washed with water and dried with $MgSO_4$, and the solvent was removed by a rotoevaporator. Most of the naphthalene was sublimed out of the crystalline product (45 °C (0.01 Torr)), and the residue was chromatographed on silica (eluent, hexane:$CHCl_3$ 5:1). The second component to come off the column was collected to give 6.35 g (98% based on sodium naphthalenide) of bright yellow needles: mp 116 °C; ^1H NMR ($CDCl_3$) 7.18–7.40 (m, 10 H), 6.80–6.86 (m, 1 H, H(2)), 6.53 (d, J = 15.6 Hz, 1 H, H(1)), 6.20–6.48 (m, 4 H), 6.17 (ddt, J = 14.9, 10.0, 1.3 Hz, 1 H, H(7)), 5.88 (dt, J = 14.9, 7.1 Hz, 1 H, H(8)), 3.46 (d, J = 7.1 Hz, 2H, H(9)). The compound was recrystallized repeatedly from hexane and from ethanol and sublimed (105 °C (10^{-3} Torr)) to remove trace impurities. The mp (114.0–114.5 °C) and ^1H NMR in DMSO-d_6 reported by Tolbert and Ogle[3a] are similar.

Prepared by the same procedure: (*E,E*)-1,5-Diphenyl-1,3-pentadiene (DP5) from (*E,E*)-1,5-diphenyl-5-methoxy-1,3-pentadiene, colorless crystals from hexane (at –70 °C): mp 35 °C (lit.[44] 33–35 °C); ^1H NMR ($CDCl_3$) 7.08–7.22 (m, 10 H), 6.77 (dd, J = 15.6, 10.5 Hz, 1 H, H(2)), 6.47 (d, J = 15.7 Hz, 1 H, H(1)), 6.25 (ddd, J = 15.2, 10.5, 0.6 Hz, 1 H, H(3)), 5.96 (dt, J = 15.1, 7.0 Hz, 1 H, H(4)), 3.48 (d, J = 7.0 Hz, 2 H, H(5)). This compound was prepared as an oil by Tolbert and Ogle,[3a] but the ^1H NMR compare.

(*E,E,E*)-1,7-Diphenyl-1,3,5-heptatriene (DP7) from (*E,E,E*)-1,7-diphenyl-7-methoxy-1,3,5-heptatriene, off white crystals from hexane: mp 82 °C; ^1H NMR ($CDCl_3$) 7.19–7.39 (m, 10 H), 6.78–6.83 (m, 1 H, H(2)), 6.52 (d, J = 15.6 Hz, 1 H, H(1)), 6.29–6.38 (2 H, H(3,4)), 6.19 (dd, J = 15.0, 9.9 Hz, 1 H, H(5)), 5.90 (dt, J = 15.0, 7.1 Hz, 1 H, H(6)), 3.47 (d, J = 7.0 Hz, 2 H, H(7)). Our mp is higher than that (76.0–76.5 °C) reported by Tolbert and Ogle[3a] for the major isomer in their product mixture, but the ^1H NMR compare well.

Carbanion UV Spectra. The extinction coefficients of the cesium salts were determined by titrating a solution of known concentration of the hydrocarbon in THF that was saturated with cesium tetraphenylborate with a solution of cumylcesium[21] (DP3) or (diphenylmethyl)cesium[45] (DP5, DP7, and DP9) in THF until the absorption of the base persisted. Control experiments with (diphenylmethyl)cesium (DP3) or (triphenylmethyl)cesium (DP5, DP7, and DP9) as the base gave identical values. Extinction coefficients for the lithium salts of DP3, DP5, and DP7 were obtained analogously in neat THF by deprotonation with (diphenylmethyl)lithium.[46] With DP9, addition of (diphenylmethyl)lithium to the polyene competed with the deprotonation and (triphenylmethyl)lithium[45] had to be used as the base. To complete the deprotonation within a reasonable time, the (triphenylmethyl)lithium was used in 10-fold excess. A control experiment showed that even at these high concentrations the (triphenylmethyl)lithium gave no absorbance at the λ_{max} of $DP9^-Li^+$.

All indicators and polyenes used were checked for impurities of higher acidity by comparing spectra of the cesium salts taken at almost complete deprotonation with spectra taken with an at least 20-fold excess of the neutral. They were identical for all compounds except DP9, for which a more acidic impurity was detected that gave a cesium salt with a λ_{max} of approximately 780 nm. All attempts to remove this impurity by either chromatography, recrystallization, or sublimation were unsuccessful. However, its influence on the precision of equilibrium measurements involving DP9 could be minimized by not using the parts of the spectrum above 700 nm.

Carbanion NMR Spectra. All NMR samples containing (diphenylpolyenyl)cesium were prepared inside an argon-filled glovebox. An 0.1 M stock solution of (triphenylmethyl)cesium was prepared by reacting a solution of excess triphenylmethane in THF-d_8 with cesium metal. For the generation of catalytic amounts of the cesium diphenylpolyenyls, a solution of ca. 0.1 mmol of the diphenylpolyene hydrocarbon in 1 mL of THF-d_8 was placed in the NMR tube and 20 μL of the base solution was added. For complete deprotonation, ca. 50 μmol of the diphenylpolyene was added to 1 mL of the base solution and the resulting mixture was transferred to the NMR tube. The NMR tubes were fitted to a vacuum stopcock with an O-ring adaptor, taken out of the box, and sealed under vacuum. NMR spectra were recorded at 22 °C on a 500-MHz instrument and at –20 °C on a 300-MHz instrument.

Transmetalation Equilibria. The procedures used in this study have been described in detail elsewhere;[45] however, some changes are noted. All solutions containing DP3, DP5, DP7, or DP9 were saturated with cesium tetraphenylborate to suppress the dissociation into free ions. Sufficient amounts of the hydrocarbons were weighed in to keep the conversion to the cesium salts below 50% for both compounds involved in the equilibrium. The concentrations of the cesium salts in the equilibrium mixtures were determined by a least-squares fit between the two spectra of the individual cesium salts and the spectrum of the equilibrium mixture. Temperatures were determined with a thermoelement placed at the height of the sample beam inside a 0.1-cm cell filled with triglyme. The thermodynamic parameters were derived from measurements done at 25, 15, 5, –10, and –20 °C.

Dissociation Equilibria. Using the same techniques as for the transmetalation equilibrium measurements, spectra for various concentrations of the cesium salts of DP3, DP5, DP7, and DP9 in neat THF were recorded in cells of 0.1-cm and 1-cm pathlength. Each spectrum in neat THF was dissected into the contributions of the contact ion pair and free ion spectrum by a least-squares fit, taking the spectrum of the cesium salt in THF saturated with cesium tetraphenylborate as the spectrum of the ion pair and the spectrum of the lithium salt in THF as a model for the free ion. The best spectral fits were obtained with the spectra of the lithium salts offset to longer wavelengths by 2.8 (DP3), 3.6 (DP5), 3.2 (DP7), and 4.0 nm (DP9). These values were used to obtain the λ_{max} reported for the free ions in Table 1.

Acknowledgment. This research was supported in part by NIH Grant No. GM-30369.

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