Lithium and Cesium Ion-Pair Acidities of Some Terminal Acetylenes and Aggregation in Tetrahydrofuran[1]

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The equilibrium lithium acidities in THF have been determined for 4-ethynylbiphenyl, EB (pK 21.5−22.3), 3,3,3-triphenylpropyne, TPP (pK 22.3−22.7), and 1-ethynyladamantane, EA (pK 23.7). Ion pairs of (4-ethynylbiphenylyl)lithium are aggregated in the concentration range from 10^{-4} to 10^{-3} M, with an average aggregation number of 2.5. (3,3,3-Triphenylpropynyl)lithium ion pairs are partially aggregated at concentrations from 10^{-5} to 10^{-3} M; the average aggregation number is 1.2. Cesium acidities in THF have been determined for 3,3,3-triphenylpropyne (pK 29.1−29.9) and 1-ethynyladamantane (pK 31.56). The average aggregation number of (3,3,3-triphenylpropynyl)-cesium ion pairs is 6.2 at concentrations of 10^{-4}−10^{-3} M.

Introduction

The alkali metal derivatives of organic compounds of various types have been shown to exist as aggregates of ion pairs—dimers, trimers, tetramers, and higher clusters—in solvents of low polarity and in the solid state.[2,3] However, the structures of acetylene salts have been studied much less than that of other types of organoalkali compounds. Theoretical calculations[4,5] for simple organolithium compounds suggest that in comparison to vinyl or alkyl derivatives ethynyllithium has effectively lower electron density between C_α and Li atoms that corresponds to greater ionic character of the carbon−lithium bond. This difference could be attributed to the strong increase in s character of the carbanion lone pair between sp^3 or sp^2 and sp hybridization. These results were the basis for the opinion that the salts of acetylenes are highly ionic compounds, and less attention has been paid to the study of their association and aggregation.

Recently, however, the X-ray structure analysis of (*tert*-butylethynyl)lithium showed that it may exist in the solid state in two forms: tetrameric and dodecameric aggregates of ion pairs.[6] Other evidence of the aggregation of lithiated acetylenes was provided for (*tert*-butylethynyl)lithium and (phenylethynyl)lithium in THF by low-temperature ^{13}C NMR and cryoscopy. (*tert*-Butylethynyl)lithium was shown by NMR to exist as a nonfluxional tetramer in 1.5 M THF solution below −80 °C.[7] Further studies[8] have shown an equilibrium at 0.75 M between the dimer and tetramer at low temperatures. At −100 °C, the mixture contains both, but increasing the temperature to −60 °C causes an increase in the content of tetramer. The equilibrium constant for eq 1 was found to be $K = 5 \times 10^{-4}$ M^3 at −80 °C.

$$2\ R_2Li_2(THF)_4 \rightleftharpoons R_4Li_4(THF)_4 + 4\ THF \qquad (1)$$
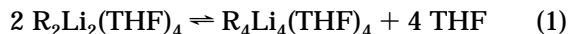
These results are consistent with an average aggregation number of 2.9 for (*tert*-butylethynyl)lithium in 0.1

M solution at −108 °C, obtained from the freezing point depression of THF.[9] (Phenylethynyl)lithium was found to be dimeric in THF below −100 °C both by cryoscopic[9] and NMR[10] studies. Cryoscopic measurements[9] have shown that many organolithium compounds that are tetrameric at ambient temperature exist as dimers near the freezing point of THF.

Not much is known about the quantitative acidity of acetylenes. Since they are quite weak acids, they allow only relative acidity measurements using indicator techniques. Reported acidity values for some aryl- and alkylacetylenes differ by as much as 8 pK units, depending on the solvent and counterion. For example, pK values for phenylacetylene were reported to be 23.2 in cyclohexylamine with lithium cation,[11] 28.7[12] and 29.1[13] in DMSO with potassium counterion, and 31.1[14] with [2.1.1]cryptated lithium in THF.

We report here lithium and cesium ion pair acidities and the aggregation states of salts of 4-ethynylbiphenyl (EB), 3,3,3-triphenylpropyne (TPP), and 1-ethynyladamantane (EA) in THF solution in the concentration range 10^{-5}−10^{-3} M at 25 °C. Ion pair acidities are defined as the transmetalation equilibrium (2); the resulting ΔpKs

$$Ind^-M^+ + AH \overset{K}{\rightleftharpoons} IndH + A^-M^+ \qquad (2)$$

$$\Delta pK = -\log K,\ pK(AH) = pK(IndH) + \Delta pK$$

are converted to absolute numbers[15] by setting the pK of fluorene equal to its ionic ΔpK of 22.9 (per hydrogen) measured in DMSO.[12]

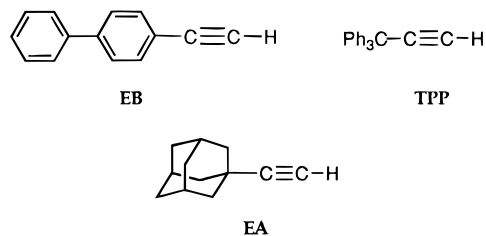[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

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EB   **TPP**

EA

Results and Discussion

Since the salts of acetylenes, A^-M^+, have no accessible electronic absorption spectra, the equilibrium constants for reaction 2 were found from the decrease of spectral absorption of the salts of indicator acids Ind^-M^+ upon the addition of acetylene AH ("single indicator technique"). This procedure requires high purity of materials and solvent since contaminants (principally traces of water) may quench the indicator carbanions, also causing a decrease of the absorption. Thus, precautions were taken to provide rigorous elimination of moisture. The decrease in the absorption due to the moisture in the compounds studied and on the surface of the sample container was evaluated in control experiments, and the necessary corrections were made. When possible, acidity measurements were done relative to two to three indicators, and reproducibility within such cross-measurements is evidence for the absence of significant systematic error. This procedure has been shown to give reproducible results with good precision.[16]

Lithium Acidity. The equilibrium acidities of EB and TPP with lithium as counterion were measured relative to the indicator acids 9-benzylfluorene (pK 21.36)[15] and 9-methylfluorene (pK 22.46);[17] the indicator for EA was 9-*tert*-butylfluorene (pK 24.41).[17] In each experiment the initial concentration of the indicator salt (Ind^-Li^+) as well as the amounts of acetylene added were varied to provide a variation in the concentration of the acetylene salt (A^-Li^+). It was shown earlier[15] that the dissociation constants of lithium salts of typical indicator CH-acids (including substituted fluorenes) in THF are relatively constant at 1×10^{-5} M. This value is sufficiently large that eq 2 can be effected by the much lower dissociation of the acetylene salts discussed below. Corrections were made as appropriate considering the acetylene salts to be effectively undissociated. The observed pK values of 4-ethynylbiphenyl, corrected this way, were found to still be dependent on the total concentration of its lithium salt (Table 1). As the salt concentration is increased the observed pK value decreases; the overall change in the concentration range from 3.4×10^{-5} to 4.6×10^{-4} M is from 22.3 to 21.5 pK units. This behavior indicates that the ion pairs are aggregated into higher ionic clusters[18] —dimers, tetramers, etc. (eq 3).

$$n(A^-M^+) \rightleftharpoons (A^-M^+)_n \qquad (3)$$
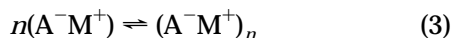
This process diminishes the amount of monomeric ion pairs and displaces the equilibrium (2) toward the right, increasing the apparent acidity of the compound studied.

The average aggregation number of ion pairs $\bar{n}$ is given by the slope of a plot of the observed pK *vs.* the logarithm of formal concentration $\{A^-M^+\}$ of the corresponding salt;

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Table 1. Lithium Ion-Pair Acidity of 4-Ethynylbiphenyl in THF at 25 °C

run	$\{EBLi\}^a$ (10^{-4} M)	p$K_{exp}{}^b$	p$K_{corr}{}^c$
1	0.344	22.35	22.28
2	0.905	21.99	21.91
3	1.550	21.79	21.69
4	0.354	22.20	22.11
5	2.714	21.85	21.75
6	1.780	21.89	21.81
7	2.715	21.77	21.65
8	4.134	21.67	21.56
9	4.640	21.66	21.53
10	2.111	21.63	21.56
11	3.376	21.61	21.51

^{a} Total concentration of (4-ethynylbiphenylyl)lithium. ^{b} Points 1−4 measured against 9-benzylfluorene as indicator, points 5−11 against 9-methylfluorene. ^{c} Corrected for the dissociation of indicator salt to free ions.
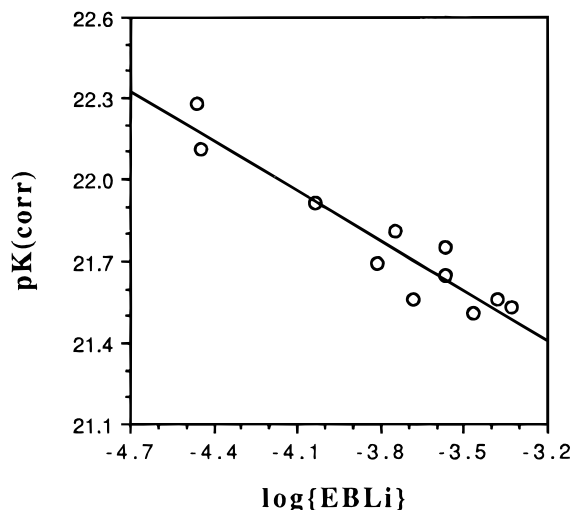

Figure 1. The plot of the corrected lithium acidity of 4-ethynylbiphenyl *vs.* the logarithm of overall concentration of its lithium salt. The data are taken from Table 1. The line shown is the least-squares fit; number of points $n = 11$; correlation coefficient $r = 0.94$, standard deviation $s = 0.087$. Slope $b = -0.605$; standard deviation of slope $s = 0.070$.

this slope is equal[18] to $(1 - \bar{n})/\bar{n}$. The corresponding plot for the lithium pK of 4-ethynylbiphenyl is shown in Figure 1.

The slope of the least-squares linear correlation gives an average aggregation number of 2.5 ± 0.4, suggesting that its lithium salt exists in THF solution mostly as ion pair dimers at the concentrations studied. This conclusion is consistent with the observations that the lithium salt of phenylacetylene is also mostly dimeric in THF.[9,10] However, it is remarkable that the dimers persist as the major species even at concentrations as low as 10^{-4} M. The structures of such dimers should be similar to that of (*tert*-butylethynyl)lithium, which was shown by X-ray structure analysis[6] to exist in the solid state as a stack of 2 or 6 dimeric units of structure **1** turned by *ca.* 90°:

1
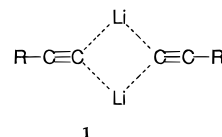
Both tetrameric and dodecameric elementary units include two molecules of THF per lithium cation such that each lithium is tetracoordinate.
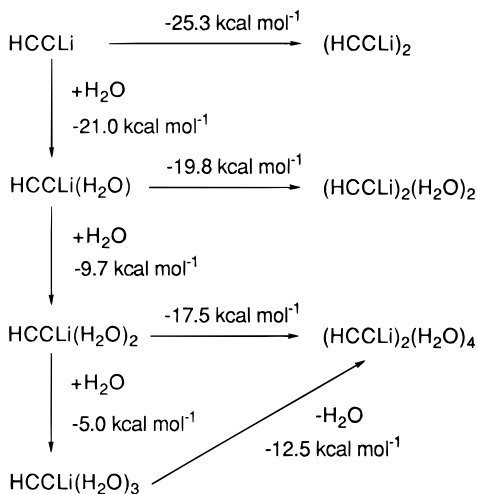
Table 2. Summary of *ab Initio* Calculations (RHF/6-31+G*) for Ethynyllithium, Its Dimer, and Their Complexes with Water Molecules

| species	point group	total energy (-au)
HCCLi	C_∞	83.701 49
HCCLi(H$_2$O)	C_{2v}	159.752 64
HCCLi(H$_2$O)$_2$	C_{2v}	235.785 84
HCCLi(H$_2$O)$_3$	C_{3v}	311.811 51
(HCCLi)$_2$	C_{2h}	167.483 54
(HCCLi)$_2$(H$_2$O)$_2$		319.568 51
(HCCLi)$_2$(H$_2$O)$_4$		471.627 47

Scheme 1. Chart of Solvation and Aggregation Energies for Ethynyllithium As Obtained from *ab Initio* RHF/6-31+G* Calculations. Dimerization Energies Are per Mole of Monomer

HCCLi $\xrightarrow{\text{-25.3 kcal mol}^{-1}}$ (HCCLi)$_2$

+H$_2$O
-21.0 kcal mol^{-1}

HCCLi(H$_2$O) $\xrightarrow{\text{-19.8 kcal mol}^{-1}}$ (HCCLi)$_2$(H$_2$O)$_2$

+H$_2$O
-9.7 kcal mol^{-1}

HCCLi(H$_2$O)$_2$ $\xrightarrow{\text{-17.5 kcal mol}^{-1}}$ (HCCLi)$_2$(H$_2$O)$_4$

+H$_2$O
-5.0 kcal mol^{-1}

-H$_2$O
-12.5 kcal mol^{-1}

HCCLi(H$_2$O)$_3$

We undertook *ab initio* calculations of ethynyllithium, HCCLi, its dimer, and corresponding complexes with H$_2$O as model systems to assess the energetics of solvation and aggregation processes. Calculations were performed at the Hartree−Fock level with the standard basis set 6-31+G* using the Gaussian92 program package.[19] Full geometry optimizations were carried out under the indicated symmetry restraints. The results of the calculations are summarized in Table 2.

The optimized structures for ethynyllithium dimer and that solvated by two and four molecules of water are presented in Figure 2. Optimization of the unsolvated species with C_{2h} symmetry yielded a structure in which each lithium cation is stabilized by π-interaction with the triple bond of ethynyl anion, resulting the geometry shown in Figure 2a. The coordination of each lithium atom by one water molecule gives only small changes in geometry, the C−Li bonds being lengthened by 0.03−0.1 Å and bending of acetylenyl moieties from coaxiality reduced from 52° to 47° (Figure 2b). The solvation by the next two water molecules overcomes the interaction between lithium and the triple bond, and the structure acquires D_{2h} symmetry, expected from X-ray data for (*tert*-butylethynyl)lithium aggregates,[6] as shown in Figure 2c.

A chart of the energy transitions among the different species is presented in Scheme 1; the interaction energies are not corrected for zero-point vibrational energies (ZPE).

(19) Gaussian 92/DFT, Revision G.1: Frisch, M. J.; G. W. Trucks; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; M. W. Wong; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; E. S. Replogle; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A., Gaussian, Inc.: Pittsburgh PA, 1993.
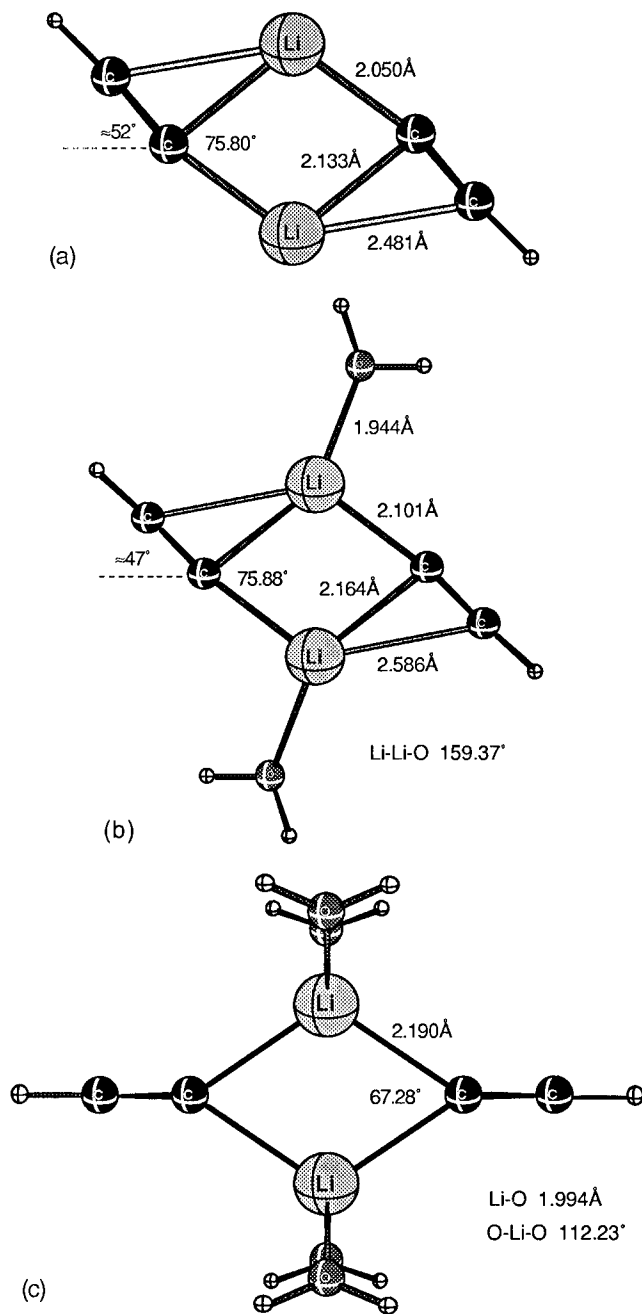
Figure 2. Optimized structures of ethynyllithium dimer (a) and its complex with two water molecules (b) and four water molecules (c) as obtained from RHF/6-31+G* *ab initio* calculations.

Scheme I implies that dimerization is favored for unsolvated ethynyllithium and at all levels of solvation, although successive addition of water molecules decreases the energetic gain in this process. Note also that the transition from trisolvated ethynyllithium to tetrasolvated dimer is favored entropically because of the release of a water molecule. The association energies of water molecules by ethynyllithium decrease in the order first ≫ second > third; that is, the binding of the first molecule is much stronger than that of second and third (−21.0, −9.7, and −5.0 kcal mol^{-1} respectively). This trend was also found in *ab initio* calculations for solvation of methyllithium by water and ammonia.[20,21] The at-

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**Table 3. Lithium Ion-Pair Acidity of
3,3,3-Triphenylpropyne in THF at 25 °C**

run	{TPPLi}[a] (10^{-5} M)	pK_{exp}[b]	pK_{corr}[c]
1	0.893	22.64	22.57
2	3.007	22.50	22.42
3	1.172	22.80	22.72
4	5.108	22.70	22.63
5	10.03	22.57	22.48
6	0.700	22.82	22.75
7	2.510	22.55	22.47
8	51.24	22.39	22.37
9	82.12	22.35	22.33

[a] Total concentration of (3,3,3-triphenylpropynyl)lithium. [b] Measured against 9-methylfluorene as indicator. [c] Corrected for the dissociation of indicator salt to free ions.

tachment of a third solvent molecule is even endergonic (by 2.8 kcal mol^{-1} for water), apparently due to higher steric requirements for methyllithium compared to ethynyllithium. It was also shown previously[22] that the energies of solvation by the first molecule of water are remarkably constant for lithium compounds with first-row elements (or hydrides where applicable), at -20.0 ± 1.2 kcal mol^{-1} (excluding ZPE, which averages $+2.0$ kcal mol^{-1}). The energy of coordination of the first water molecule to ethynyllithium, 21.0 kcal mol^{-1} found in the present work is close to this value, consistent with the high ionic character of lithium–carbon bonds.

Thus, the study of this simpified model system suggests that dimerization of lithium acetylide is a favorable process both for unsolvated ion pairs and for complexes with different numbers of solvent molecules. This result is in good accord with the experimental data.

The measured acidity of TPP shows only moderate dependence upon the total concentration of its lithium salt (Table 3), the pK ranging from 22.7 to 22.3 at concentrations from 7×10^{-6} to 8×10^{-4} M. The slope of the least-squares fit to the plot of the lithium acidity of TPP *vs.* the salt concentration (Figure 3) corresponds to an average aggregation number of 1.19 ± 0.07, implying the presence of only a small amount of aggregates. Plotted as an equilibrium between monomer and dimer,[23] the data give substantial scatter but do give the pK of the monomer as 23.6 ± 0.1 and $K_d = (9 \pm 4) \times 10^2$ M^{-1}. The difference in the extent of aggregation of EB and TPP may be attributed to the bulky triphenylmethyl moiety in the latter compound that disfavors aggregation for steric and entropic reasons.

The lithium acidity of 1-ethynyladamantane defied the same type of quantitative analysis as EB and TPP because of experimental difficulties. The equilibrium between the indicator (9-*tert*-butylfluorene) and EA is extremely slow, and the pK could only be estimated as 23.7 ± 0.3. No systematic dependence of pK upon the concentration of (1-ethynyladamantyl)lithium was observed.

Cesium Acidity. Acidity measurements with cesium as counterion were done only for TPP and EA because the cesium salt of 4-ethynylbiphenyl is insoluble in THF. Diphenylmethane (pK_a 33.25), triphenylmethane (pK_a 31.26), and biphenylyldiphenylmethane (pK 30.07) were

(21) Dixon, R. E.; Streitwieser, A.; Laidig, K. E.; Bader, R. F. W.; Harder, S. *J. Phys. Chem.* **1993**, *97*, 3728−36.
(22) Kaufmann, E.; Tidor, B.; Schleyer, P. v. R. *J. Comput. Chem.* **1986**, *7*, 334−344.
(23) Ciula, J. C.; Streitwieser, A. *J. Org. Chem.* **1992**, *57*, 431−2. Correction: *Ibid.* 6686.
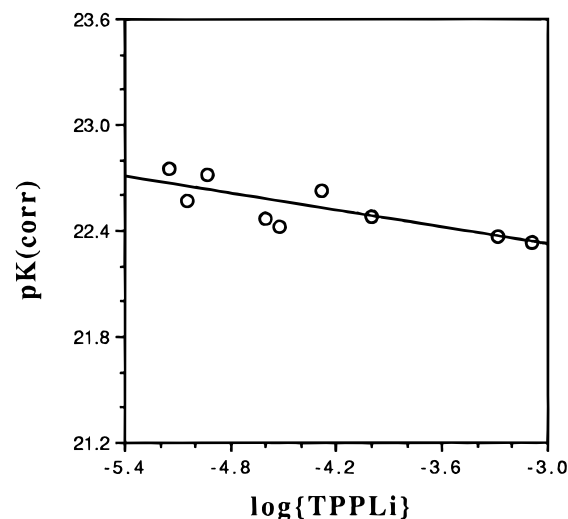
Figure 3. Plot of the corrected lithium acidity of 3,3,3-triphenylpropyne *vs.* the logarithm of overall concentration of its lithium salt. The data are taken from Table 3. The line shown is the least-squares fit; number of points $n = 9$; correlation coefficient $r = 0.80$, standard deviation $s = 0.096$. Slope $b = -0.162$; standard deviation of slope $s = 0.046$.

**Table 4. Cesium Ion-Pair Acidity of
3,3,3-Triphenylpropyne in THF at 25 °C**

run	{TPPCs}[a] (10^{-4} M)	pK[b]	run	{TPPCs}[a] (10^{-4} M)	pK[b]
1	3.037	29.38	9	1.704	29.40
2	3.214	29.39	10	2.360	29.35
3	0.907	29.71	11	3.024	29.16
4	1.283	29.63	12	4.136	29.14
5	1.380	29.58	13	0.634	29.89
6	1.852	29.53	14	1.185	29.78
7	2.329	29.47	15	1.186	29.59
8	2.355	29.45	16	2.511	29.40

[a] Total concentration of 3,3,3-triphenylpropynyl. [b] Measured against triphenylmethane as indicator.

used as indicators.[24] Since the dissociation constants of cesium ion pairs (typically 10^{-8} M for fluorenyl derivatives)[15] are lower than that for lithium salts, the presence of free ions may be neglected and no correction is required at the concentrations used.

The variation of the pK of 3,3,3-triphenylpropyne with concentration again indicates aggregation of the cesium salt ion pairs (Table 4). The average aggregation number as determined from the slope of the least-squares linear fit (Figure 4) is 6.2. This value should be regarded as an estimate because within one standard deviation of the slope it may range from 4 to 14. However, it does have precedent since it has been shown that organic salts can exist in hexameric forms,[3] as a stack of either three dimers or two cyclic six-membered trimers. The experimental values of the pK for TPP vary from 29.9 to 29.1 at concentrations of 6×10^{-5} to 4×10^{-4} M.

The cesium salt of 1-ethynyladamantane exists as monomeric ion pairs in THF at concentrations below 10^{-4} M; its pK of 31.56 ± 0.03 exhibits no dependence on the concentration of the cesium salt (Table 5). At concentrations from 10^{-4} to 7×10^{-3} M the pK values vary chaotically, and at higher concentrations precipitation becomes visible as an opalescence of the solution. Apparently, the solubility of (1-ethynyladamantyl)cesium is about 10^{-4} M, and measurements of pK of EA above this concentration are meaningless.

(24) Streitwieser, A.; Ciula, J. C.; Krom, J. A.; Thiele, G. *J. Org. Chem.* **1991**, *56*, 1074−1076.
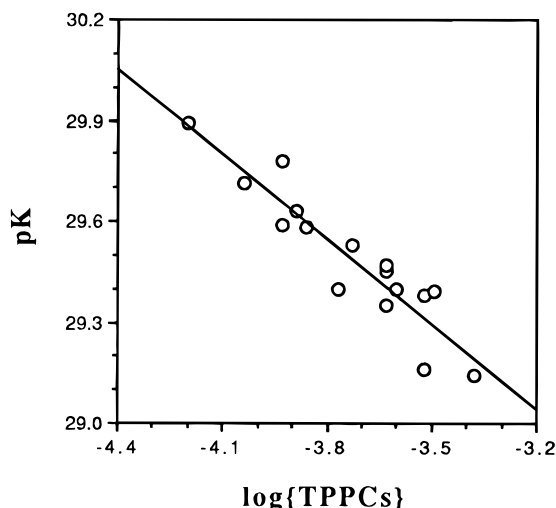
Figure 4. Plot of the cesium acidity of 3,3,3-triphenylpropyne *vs.* the logarithm of overall concentration of its cesium salt. The data are taken from Table 4. The line shown is the least-squares fit; number of points $n = 16$; correlation coefficient $r = 0.93$, standard deviation $s = 0.080$. Slope $b = -0.840$; standard deviation of slope $s = 0.092$.

**Table 5. Cesium Ion-Pair Acidity of
1-Ethynyladamantane in THF at 25 °C**

run	{EACs}[a] $(10^{-5}$ M)	pK[b]	run	{EACs}[a] $(10^{-5}$ M)	pK[b]
1	0.756	31.60	8	10.60	31.52
2	2.802	31.57	9	10.31	31.49
3	3.739	31.59	10	9.433	31.55
4	2.062	31.56	11	7.054	31.66
5	4.944	31.61	12	8.220	31.49
6	10.71	31.56	13	8.208	31.58
7	10.34	31.55	14	10.43	31.55

[a] Total concentration of (1-ethynyladamantyl)cesium. [b] Points 1−3 measured against biphenylyldiphenylmethane, points 4 and 5 against triphenylmethane and points 6−14 against diphenylmethane as indicator.

**Table 6. Ion-Pair Acidities and Average Aggregation
Numbers for Ion Pairs in THF**

	Li$^+$		Cs$^+$	
compd	pK	$\bar{n}$[a]	pK	$\bar{n}$[a]
4-ethynylbiphenyl	21.5−22.3	2.5		
3,3,3-triphenylpropyne	22.3−22.7[b]	1.19	29.1−29.9	6.2
1-ethynyladamantane	23.7		31.56	1

[a] Average aggregation number for ion pairs. [b] pK of monomer = 22.6 ± 0.1.

Comparison of average aggregation numbers for cesium and lithium salts of the compounds studied (Table 6) shows that acetylenes follow the general pattern that the cesium salts of organic compounds are usually more aggregated than related lithium ones.[17,25] Direct comparison is possible only for TPP for which the cesium salt is highly aggregated, whereas the lithium salt is mainly monomeric. It is consistent with this generalization that the cesium salt of EB is insoluble in THF, since the lithiated derivative exhibits considerable aggregation. Although the lithium salt of 1-ethynyladamantane could not be directly established to be monomeric it may be expected to be monomeric since the cesium salt is established as monomeric at these concentrations.

Comparison of lithium and cesium acidities (Table 6) shows that they differ by about 8 pK units for 1-ethyny-

ladamantane. For TPP the observed values differ by 7 units, but since the cesium pK for monomeric ion pairs should be higher than that for the observed aggregated species the difference for the corresponding monomers is probably also about 8 pK units. Organocesium salts are generally contact ion pairs in THF; the lithium acetylenic ion pairs are thus undoubtedly also contact ion pairs, held more tightly by the increased electrostatic interaction of the anion with the smaller lithium cation.

The argument can be put in terms of ionic dissociation. Ion pair dissociation constants of the cesium salts of the delocalized indicators are of the order of 10^{-8} M.[15] The dissociation constants of cesium salts of more delocalized carbanions are of greater magnitude;[26] thus, 10^{-8} M is an upper limit for the dissociation of the cesium acetylides. The lithium acidity scale is defined by the solvent separated ion pairs of the indicator salts whose dissociation constants are 10^{-5} M; the 8 pK unit difference then implies that the dissociation constants for the lithium acetylides have an upper limit of 10^{-13} M, or 10^{-5} that of the cesium salts. This difference is again consistent with both salts being contact ion pairs involving localized carbanions.

Within a given scale the relative acidities of the three compounds studied are quite close. The lithium acidity of EB is only about 1 pK unit more acidic than EA. The lithium pK of EB for the monomer must be higher than 22.3 and probably not far from that for the monomer of TPP. This result is consistent with an inductive effect since TPP has three aryl groups one carbon farther removed. Extension of these principles to the cesium salts suggests that the pK of TPP for the monomeric cesium salt should be about 1 pK unit less than that for EA or about 30.5 pK units, not much more than that measured for the aggregate. Similarly, the cesium pK of EB, if it could have been measured, would also be about 30.5. EB should be somewhat more acidic than phenylacetylene, and this value fits in well with that for the [2.1.1]cryptated lithium salt of phenylacetylene, 31.1.[14] It also means that the reported lower values for phenylacetylene in DMSO[12,13] do not correspond to the dissociated ions but are those of ion pairs.

Nevertheless, these results show that the electronic effects of the substituent play a relatively minor role in the acidity of acetylenes. This conclusion is also consistent with the observation that ρ-parameter in the correlation of the potassium pK of arylacetylenes in DMSO *vs.* $\sigma°$ is only 3.5,[13] almost four times less than that for toluenes.

Experimental Section

General. Melting points were determined on a Buchi melting point apparatus and are uncorrected. NMR spectra were taken on Brucker AMX-300 and AMX-400 spectrometers in the FT mode.

Materials. The compounds studied were prepared according to known methods. 4-Ethynylbiphenyl was prepared by the reaction of 4-acetylbiphenyl with PCl$_5$ in dry pyridine:[27] mp 88−88.5 °C (lit.[27] mp 88−89 °C); ^{1}H NMR in CDCl$_3$ δ 7.60−7.37 (m, 9H), 3.14 (s, 1H). 3,3,3-Triphenylpropyne was prepared by the reaction of ethynylmagnesium bromide with

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triphenylmethyl chloride in THF:[28] mp 82–83 °C (lit.[28] mp 83 °C); ^{1}H NMR in CDCl$_3$ δ 7.36–7.25 (m, 15H), 2.74 (s, 1H); ^{13}C NMR in CDCl$_3$ δ 144.8, 129.1, 128.1, 127.0, 89.8, 73.5. 1-Ethynyladamantane was prepared by the addition of vinyl bromide to 1-bromoadamantane in the presence of FeCl$_3$ in dichloromethane–hexane mixture as solvent and consequent elimination of HBr by potassium *tert*-butoxide in DMSO:[29] mp 81–82 °C (lit.[29] mp 82–83 °C); ^{1}H NMR in CDCl$_3$ δ 2.10 (s, 1H), 1.96 (septet, 3H), 1.89 (d, 6H; J = 3 Hz), 1.69 (t, 6H; J = 3 Hz).

4-Ethynylbiphenyl and 1-ethynyladamantane were purified via their silver salts according to the following general procedure. The calculated equimolar amount of silver nitrate was dissolved in the minimum amount of distilled water, and 25% aqueous ammonia was added dropwise. Addition was considered complete when the brown precipitate of silver oxide formed by addition of 1 equiv of ammonia dissolved in excess ammonia with formation of a clear solution. The acetylene was dissolved in a 2-fold excess of 95% ethanol, and the solution of the ammin complex of silver nitrate was added. The mixture was stirred for 2 h while avoiding exposure to light. The white to golden precipitate (depending on the purity of starting material) was filtered, washed thoroughly with acetone and hexane, and decomposed by vigorous stirring overnight in a mixture of 10% HCl and ether. The ethereal layer was washed with sodium carbonate solution and twice with water, dried over magnesium sulfate, and evaporated to yield the purified product.

3,3,3-Triphenylpropyne was purified by column chromatography on silica gel, with gradient elution in the range hexane to 3% ethyl acetate in hexane.

Final purification of compounds was achieved by repeated sublimation in vacuum, 10^{-2} mmHg for EB and TPP and 20 mmHg for EA, since the latter is a highly volatile solid.

9,9,10-Trimethyl-9,10-dihydroanthracene was prepared by addition of a solution of methyllithium solution to 9,9-dimethylanthrone in THF followed by reduction of the alcohol by hydriodic acid in glacial acetic acid:[30] mp 78–78.5 °C (lit.[30] mp 78–79 °C). The compound was purified by crystallization from ethanol and vacuum sublimation.

The purity of the compounds was confirmed by a combination of TLC, melting point, and NMR spectra. The purification of THF was described earlier.[25]

Standard Bases. For deprotonation of the indicator acids, the lithium salt of 9,9,10-trimethyl-9,10-dihydroanthracene and the cesium salts of diphenylmethane and cumene were used as standard bases. The cesium salts were prepared by direct reaction of diphenylmethane and bicumyl, respectively, with cesium metal in THF.[25] The lithium base was prepared by reaction of lithium diisopropylamide with 9,9,10-trimethyl-9,10-dihydroanthracene in THF solution.[31] Standard bases were prepared as *ca.* 0.1 M solutions and stored in a refrigerator inside the glovebox. The solutions of the bases were checked for decomposition prior to measurement by comparison of the UV spectra of standards, and fresh stock solutions were prepared as necessary.

Acidity Measurements. Details of the spectrophotometric acidity determinations in an argon-filled glovebox were described previously.[25] A typical "single indicator" experiment included the following steps. The spectrophotometric cell was pretreated for 1–2 h (1 d in measurements of the lithium acidity of EA) with a 10^{-4}–10^{-3} M THF solution of standard base to remove traces of moisture and impurities on the inner surfaces of the cell and in the solvent. A measured sample of indicator was added to the cell and left to react with the base. The reaction was controlled spectrophotometrically and was generally complete in 10–15 min except for the formation of (9-*tert*-butylfluorenyl)lithium, which took 12–24 h. The spectrum of the indicator salt solution was recorded, and a measured sample of the compound under study was added. Equilibration in most cases took 15–30 min as judged by the constancy of the spectrum with time, but the equilibrium between 9-*tert*-butylfluorene and EA was only established after 7–8 days. The spectrum of the equilibrium mixture was recorded, and the concentration of the salt of the studied acid was determined as a decrease of concentration of indicator salt. Note that this assumption is true only if the impurities in the added compound and on the surface of its container (Pyrex microbeaker) do not quench the indicator salt. This quenching was evaluated in control experiments with empty microbeakers, and with indicator salts with basicity low enough not to deprotonate the acids studied, but to react with residual moisture in them. The corresponding corrections were made in the calculations of the equilibrium constants.

Analysis of errors suggests that in most cases both systematic and stochastic uncertainties of pK values are within ±0.1 units. Statistical treatment of correlations was carried out on the 95% confidence level. Uncertainties were assigned as 1 standard deviation.

Supporting Information Available: Z-matrices for the *ab initio* calculations (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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