Carbanion Ion Pairs and Triplets†

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Carbanions are among the important intermediates in organic chemistry. They may be defined as negatively charged species in which a substantial fraction of the charge is associated with one or more carbon atoms. Carbanions may generally be derived from an appropriate carbon acid by heterolytic cleavage of a proton from a C–H bond. Accordingly, the stability of a carbanion can be characterized as the acidity of the corresponding carbon acid. For about the past 25 years our laboratory has worked on quantitative measurements of such carbon acidities. The subject is conveniently divided into eight subheadings by the following three alternative pairs of categories:

Equilibrium	Ionic	Delocalized carbanions
Kinetic	Ion pair	Localized carbanions

Each is now a large subject involving a vast literature. We will concentrate here on equilibrium ion-pair acidities involving delocalized carbanions with emphasis on new results regarding dianions. These results have an important bearing on the structures and stabilities of dimetalated compounds.

Equilibrium Ion-Pair Acidities

Much of our work has involved the proton-transfer equilibria of cesium salts:

$$R^-Cs^+ + R'H \rightleftharpoons RH + R'^-Cs^+ \quad (1)$$

At least one of the cesium salts has a distinctive visible spectrum that permits determination of the equilibrium constant. Much of our work has been done in cyclohexylamine (CHA) solution in which the cesium salts exist primarily as contact ion pairs. By making a number of such measurements over a wide range, a scale of relative acidities has been developed. For convenience, these relative acidities have been converted to "absolute p*K*s" for an approximate aqueous standard state based on the value of 18.49 for 9-phenylfluorene determined by H_ measurements in aqueous sulfolane.[1] We refer to such absolute values as pK_{CsCHA} as defined by

$$pK_{CsCHA} = 18.49 - \log K \text{ (with 9-phenylfluorene)} \quad (2)$$

The pK_{CsCHA} values thus correspond approximately to ionic pK_a values for aqueous solutions, at least for delocalized carbanions. This relationship has recently been confirmed by comparison of pK_{CsCHA} for cyclopentadiene with a direct determination of the pK_a for aqueous cyclopentadiene; the values are 16.25 and 15.6, respectively.[2] Note that all p*K* values are statistically corrected to refer to the acidity per H.

Andrew Streitwieser, Jr. was born in Buffalo, NY, and spent his early years in New York City. He graduated from Stuyvesant High School and Columbia College (after an interruption of 1.5 years in the U.S. Army) and received the Ph.D. from Columbia University. After a postdoctoral year at M.I.T. as an A.E.C. fellow, he joined the chemistry faculty of the University of California, Berkeley, in 1952, where he is Professor of Chemistry.

Table I
pK_a of Organic Indicator Acids[a]

compd[b]	THF[c]	CHA	Me_2SO	DME[e]
9PhFl	(18.49)[d]	(18.49)[d]	17.9	17.55
2PI	19.10		19.4	
3,4BF	19.90	19.75		
1,2BF	20.54	20.35		
9BzFl	20.92	21.27	21.4	20.95
9MeFl	21.85	22.30	22.3	
Fl	22.41	23.04	22.9	22.3
4,5MP	22.42	22.93	22.7	
2,3BF	23.15	23.47	23.5	
9tBuFl	24.22	24.25	24.33	23.75
TPP	26.52	26.59	26.2	
PDDA	27.86	28.01		
9PX	28.50	28.49	27.7	27.7
BDPM	29.83	30.17	29.4	29.3
TPM	31.02	31.45	30.6	30.75
pBB	31.43	31.82		
TpTM	32.86	33.04		
DPM	33.01	33.41	32.6	
DoTM	33.95	34.80		

[a] The p*K* values are estimated to be accurate to ±0.1 p*K* unit and are statistically corrected to refer to a per-H basis (ref 3). [b] Abbreviations are as follows: 9PhFl, 9-phenylfluorene; 2PI, 2-phenylindene; 3,4BF, 3,4-benzfluorene; 1,2BF, 1,2-benzfluorene; 9BzFl, 9-benzylfluorene; 9MeFl, 9-methylfluorene; 4,5MP, 4,5-methylenephenanthrene; Fl, fluorene; 2,3BF, 2,3-benzofluorene; 9tBuFl, 9-*tert*-butylfluorene; TPP, 1,1,3-triphenylpropene; PDDA, 9-phenyl-10,10-dimethyldihydroanthracene; 9PX, 9-phenylxanthene; BDPM, biphenyldiphenylmethane; TPM, triphenylmethane; *p*-benzylbiphenyl; TpTM, tri-*p*-tolylmethane; DPM, diphenylmethane; DoTM, di-*o*-tolylmethane. [c] At 25 °C. [d] Assumed value to set the scale in absolute terms related to aqueous conditions (ref 3). [e] Referred to 1,1,3,3-tetraphenylpropene with an assumed value of 25.25 (statistically corrected).

A number of pK_{CsCHA} values have been determined and have recently been reviewed.[3] For many carbon acids these values can be compared to acidity measurements in dimethyl sulfoxide (Me_2SO) solution provided by the extensive work of Professor F. G. Bordwell.[4] Table I compares the ion-pair of pK_{CsCHA} values of a series of compounds having highly delocalized carbanions with the corresponding ionic pK_{Me_2SO} values. These two different sets of values are linearly correlated to an amazing degree by eq 3. The quality

$$pK_{Me_2SO} = 0.958\ pK_{CsCHA} + 0.554 \quad (3)$$

of the correlation, as shown pictorially in Figure 1, must

† This paper is based on the award address for the 1982 James F. Norris Award in Physical Organic Chemistry, sponsored by the Northeastern Section, at the 183rd National Meeting of the American Chemical Society, March 1982.

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(4) Bordwell, F. G. *Pure Appl. Chem.* **1977**, *49*, 963 and references therein.

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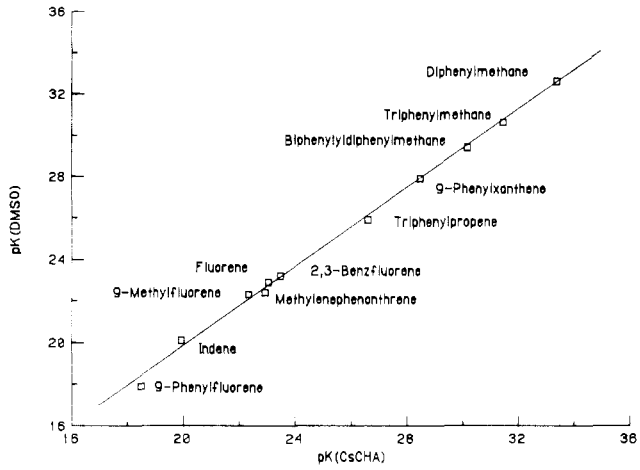


Figure 1. Correlation of cesium ion pair pKs in cyclohexylamine, pK_{CsCHA}, with ionic pKs in dimethyl sulfoxide, pK_{Me_2SO}.

mean that for a highly delocalized carbanion the electrostatic attraction to a large cation in a contact ion pair and to the dipoles of a polar solvent are affected comparably by structural change. This is an important result for it means that such highly delocalized systems provide a valuable reference set for the elucidation of specific interactions in other systems.

The same types of correlations extend to ion-pair acidities in dimethoxyethane[5] and tetrahydrofuran[6] (Table I). The close correlation between cesium ion pair acidities in cyclohexylamine and in tetrahydrofuran (pK_{THF}) is shown by eq 4, which has a correlation coefficient of 0.998.[6] Moreover, although the choice

$$pK_{CsCHA} = 1.02\ pK_{THF} - 0.31 \qquad (4)$$

of the reference system in THF, pK(9-phenylfluorene) = 18.49, is rather arbitrary, the net results coincide closely to the Me_2SO scale. At 25 °C, some of the differences in the pKs of the indicators between the two solvents are positive and some are negative; the net difference for 13 compounds is +0.04 and the average difference is 0.4.

An interesting application involves ionic acidities in CHA as defined by

$$RH \rightleftharpoons C_6H_{11}NH_3{}^+R^- \qquad (5)$$

Hence, the ion-pair acidity constant, $K = [R^-C_6H_{11}NH_3{}^+]/[RH]$, is unitless. Values of such "true" ion-pair equilibrium constants have been determined for several highly acidic hydrocarbons; an example is 1,3-diphenylindene whose ion-pair pK_{CHA} is 2.21.[8] Since the ion-pair effects are so nonspecific, we may expect the ion-pair dissociation constant of the cyclohexylammonium salt to be comparable to the lithium salt, about 10^{-10} M; thus, the true ionic acidity of 1,3-diphenylindene in CHA is approximately 12, a value that is rather close to the pK_{CsCHA} determination of 13.6.[8] This analysis shows that the magnitudes of pK_{CsCHA}, which refer to ion pairs and which were shown above to be comparable to true ionic pK_a values in water, are also comparable to the true ionic pK values in cyclohexylamine; that is, at least for highly delocalized carbon acids, the higher basicity of the amine compensates for its lower polarity compared to that of water such that ionic acidities in both solvents are comparable.

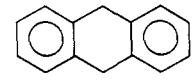
Table II
First and Second pK Values

hydrocarbon	pK^1_{CsCHA}	pK^2_{CsCHA}	$pK^1_{Me_2SO}$	$pK^2_{Me_2SO}$
1	30.3	34.1		
2	19.8	20.3	19.6	25.3
3	20.5	20.7	20.9	24.7
4	22.3	25.7	22.7	33.2
5	22.4	27.3	23.1	34.0

Dicarbanions and Ion Triplets

Dicarbanions such as those derived from carboxylic acids, $RCH{=}CO_2{}^{-2}$, β-keto esters, $CH_2{=}C(O^-)CH{=}C(OEt)O^-$, etc., have recently become important reagents, at least in the form of their lithium salt ion triplets or aggregates in ethereal solvents.[9] We plan to study their quantitative stabilities, but these systems involve oxide-type anions which introduce a significant new element into the ionic interactions. Because of this additional factor, we thought it wise to try to first understand delocalized dicarbanions in which the anionic charge does not involve heteroatoms.

One of our first such determinations was 9,10-dihydroanthracene, **1**.[10] The first acidity constant,



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pK^1_{CsCHA} = 30.3, is unexceptional, but the second, pK^2_{CsCHA} = 34.1, is remarkable for being only 3.8 pK units higher. We thought the rather low pK was in part associated with the delocalization stabilization implied by the fact that the dianion is actually anthracene dianion, but we also thought that the structure of the ion triplet was a major factor. The crystal structure of a dilithium salt of anthracene has been determined.[11] The two lithiums, each solvated by *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), are on opposite sides of the approximate ring plane, one over the central ring and one under an end ring. Simple Coulombic considerations would suggest a structure with lithiums symmetrically arranged above and below the central ring and such a structure may actually obtain in solution. The potential surface for moving the cation in such systems is rather shallow[12] and the less symmetrical structure in the crystal could readily be dictated by crystal packing or Madelung forces.

More surprises were to follow. Jon Swanson[13] recently determined the first and second acidity constants of four additional hydrocarbons, 2,2′-biindenyl (**2**),

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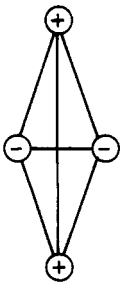
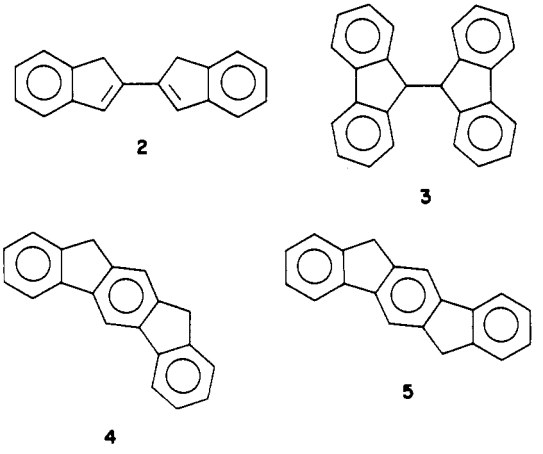


Figure 2. Coulomb interactions for a point charge model of a dication salt of a dicarbanion.

9,9′-bifluorenyl (**3**), 10,12-dihydroindeno[2,1-*b*]fluorene (**4**), and 6,12-dihydroindeno[1,2-*b*]fluorene (**5**) (Table II). In all cases, the first pK_{CsCHA} value was as expected



by comparison with other fluorene and indene compounds. The second pK_{CsCHA}, however, varied over a broad range. For **2** and **3**, $\Delta pK < 1$; indeed, for **3** the two p*K*s barely differ by more than the experimental error and the formation of the dianion is hardly more difficult than generating the monoanion. The ΔpK values for the indenofluorenes **4** and **5** are much larger.

These results can actually be rationalized by a simple consideration of Coulomb's law. Consider the collection of charges in Figure 2. The net electrostatic energy, E_{el}, is given by

$$E_{el} = \frac{1}{R_{++}} + \frac{1}{R_{--}} - \frac{4}{R_{+-}} \qquad (6)$$

in which the *R*'s are the appropriate charge–charge distances. A simple arithmetic analysis of eq 6 shows that E_{el} is negative over the range $0.14 < R_{--}/R_{++} < 6.9$; that is, the electrostatic energy is not stabilizing only when one set of charges is quite far from the other. The crucial feature is that each charge in such a collection is attracted equally to *two* opposite charges and repelled by a single like charge. In general, virtually all chemically reasonable dicarbanion ion triplet structures represented approximately by Figure 2 correspond to electrostatic stability.

Ion triplets and ion aggregates are certainly not new concepts. Charged ionic aggregates are important in the conductivity of ionic species at moderate concentrations.[14] Ion pairs and higher aggregates are well known in carbanion chemistry.[15] A number of dicarbanion ion triplet systems have been previously recognized and studied.[16] Even eq 6 itself is just the first term of a Madelung constant calculation for a crystal. Thus, neither the concept of an ion triplet as in Figure 2 nor eq 6 are particularly novel. Our contribution is simply the recognition of this simple system and its implications for interpreting and rationalizing a wide range of organic chemistry, much of which is otherwise rather puzzling.

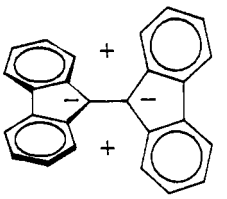


Figure 3. Ion triplet structure of dialkali cation salts of 9,9′-bifluorenyl, **3**.

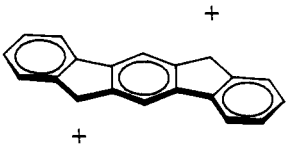


Figure 4. Ion triplet structure assumed for a dialkali salt of **5**.

The structure of a dilithium salt of **3** has been determined.[17] The two fluorenyl planes are twisted about their joining bond and two solvated lithiums are symmetrically arrayed on opposite sides of the bond midpoint. The assembly corresponds to Figure 2 and a comparable structure seems reasonable for a dicesium salt (Figure 3). The pronounced net electrostatic stabilization within such an ion triplet is such that its preparation is greatly facilitated, especially by comparison with the free dianion itself and its attendant electron repulsion.

The indenofluorenes involve a further consideration because the charge is concentrated at the 9-fluorenyl-type positions and the ion triplet is expected to have a structure as in Figure 4. In such a structure each cation is located close to a carbon having substantial negative charge, but the assembly lacks the symmetry and enhanced stabilization of Figure 2. Each cation is attracted strongly by its nearby carbanion center but much more weakly by the distant carbanion center.

The difference in the second pK_{CsCHA} values between **4** and **5** is probably associated with their relationship to *m*- and *p*-xylylene dianion, respectively. In *m*-xylylene dianion the two exocyclic positions are not conjugated, and it is produced in metalation reactions more readily than *p*-xylylene dianion.[18]

These interpretations are further supported by recent studies in Me_2SO solution (Table II).[19] For **4** and **5**, the differences between first and second p*K*s are now more than 10 p*K* units. Those rather large p*K*s suggest that in these cases the $pK^2_{Me_2SO}$ refers to dissociation to the free dianion and two cesium cations. For **2** and **3**, however, the p*K*s are only 5.7 and 3.8, respectively. In these cases, in which the two negative charges are

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concentrated more closely together, it would appear reasonable that the second pK refers to formation of the negatively charged ion pair:

$$RH^- + B^- + Cs^+ \rightleftharpoons R^{2-}Cs^+ + BH \qquad (7)$$

Dianion–cation pairs are known to be 10^2 more stable than monoanion–cation pairs.[20]

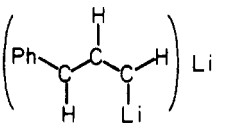
Di- and Polylithiated Compounds

The carbanions discussed above are cesium salts of delocalized dianions. There is no question that these compounds are effectively described as ion multiplets with no chemically significant degree of carbon–metal covalency. The stability of such ion multiplets was shown above to be readily explicable by classical Coulombic interactions. The essential point of these considerations is the unexpected conclusion that within an ion triplet formed from a dianion and two cations, electrostatic stabilization is enhanced *when the dianionic charges are close together*, the exact opposite result from considerations of electrostatic repulsion within a dianion itself.

These conclusions apply to the known crystal structures of dilithium salts of delocalized dicarbanions, particularly when allowance is made for crystal effects. A typical example is the dilithium salt of stilbene dianion; the structure of this compound is that in which the two lithium cations lie above and below the midpoint of a planar stilbene dianion.[21] Thus, the facile production of many di- and polylithiated reagents in organic syntheses is undoubtedly to be rationalized by similar Coulombic considerations. These reagents should be thought of less as dianions than as ion triplets or aggregates.

We now take a large jump from delocalized systems to localized ones. According to the simple Coulombic argument developed above, the ion triplet derived from a dicarbanion even with negative charge on adjacent carbons would have net electrostatic stability using normal carbon–alkali-metal bond distances. Could this approach be applied to polylithiated structures that had been thought to have localized and partially covalent bonds? Even for localized carbanions, we have argued on the basis of electron-density analyses that the C–Li bond is essentially ionic; that is, that covalency is much less than generally believed.[22] This interpretation of electron-density patterns has been challenged[23] and answered.[24] This is not the place for a full discussion of the nature of the carbon–lithium bond, but a few important points will be made. Molecular orbital calculations of organolithium compounds using small basis sets generally contain a large "superposition" error.[25] An electron-rich region, as in a carbanion lone pair, that is underdescribed by the mathematical functions of a small basis set will use the mathematical functions centered on a nearby electron-deficient lithium to aid its description. This effect is particularly evident in minimum basis set calculations and gives entirely unrealistic Mulliken populations. *Minimum basis set calculations of organolithium compounds cannot be trusted.* Moreover, unique structural effects in some organolithium compounds that had been attributed to multicenter bonding have been shown recently to derive from simple Coulombic interactions within ion pairs.[26,27] This is not to say that there is *no* carbon–lithium covalency. There is always some orbital overlap—enough, for example, to provide a mechanism for some charge transfer with spin polarization to give rise to carbon–lithium coupling constants—but the magnitude is qualitatively small compared to simple Coulombic ion-pair attraction. At this time this view is still controversial but is being increasingly supported by other workers in the field.[28,29]

Recent results show that even polylithiated organic compounds may be well approximated as tight ion multiplets. An example is given by dilithiopropene, prepared by Klein and Medlik-Balan by metalation of propylene with excess butyllithium and TMEDA.[30] The compound was formulated as a lithioallyllithium with both π- and σ-bonded lithiums. The NMR spectrum of the analogous dilithiated compound from allylbenzene indicated cis and trans hydrogens and was assigned the structure 6.[30]



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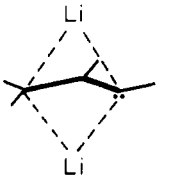

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Ab initio MO calculations at the split valence shell basis level by us[31] and by Schleyer and Kos[32] show that the minimum-energy structure of dilithiopropene as the gas-phase monomer is actually that with two π-bonded lithiums, 7. Electron-density analysis shows that the structure is essentially that of an allylidene dianion with two ionic lithium cations; that is, the compound is essentially an ion triplet that is stabilized by Coulombic interactions as represented approximately by Figure 2. This type of result now appears to be quite general. The crystal structure of a TMEDA complex of *o,o'*-dilithiobiphenyl has the bridged structure 8.[33] Many other crystal structures and related theoretical calculations show a common repetition of this general pattern.[34]

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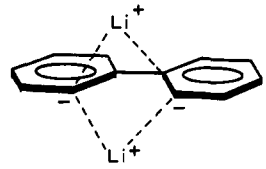

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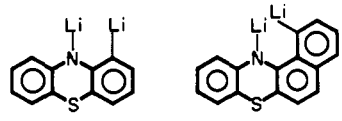
Even considered simply as a model, the ionic cluster picture of dilithioorganic compounds combined with the simple electrostatic considerations emphasized above serve to rationalize some puzzling metalation results in the literature. For example, Shirley and his colleagues reported over two decades ago that the metalation of phenothiazine with excess butyllithium gives the dilithiated compound **9**.[35] The first metalation removes



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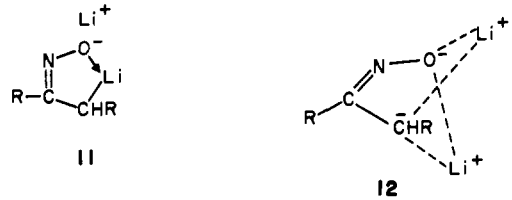
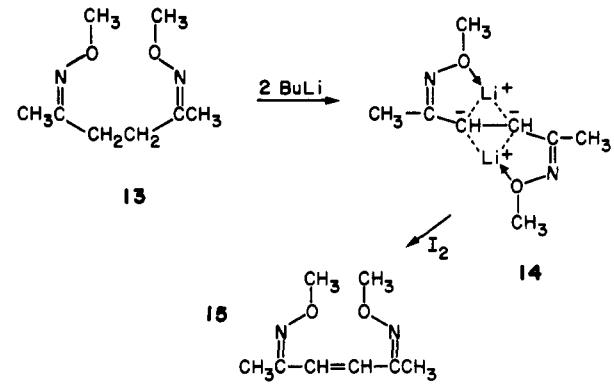
the acidic proton from nitrogen. Unexpected was the second metalation occurring so close to the first negative charge. Even more remarkable was the formation of **10** from the dimetalation of benzophenothiazine. In **10** the two lone pairs of the dianion are actually directed toward each other and should entail substantial electron repulsion. These results are now readily rationalized by the Coulombic stabilization within an ion cluster model represented by Figure 2. That is, we would interpret these structures in terms of localized ion-pair anions on nitrogen and ring carbon with associated lithium cations above and below. As in Figure 2, the electron repulsion in the dianion moiety is more than compensated by the Coulombic attraction to both cations.

Still other examples involve partially chelated lithiums. The second metalation of ketoximes occurs on the syn side of the oxime group.[36] This result was rationalized by the chelate structure **11** but is equally consistent with the ion cluster model **12**.



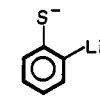
11 12

A pertinent example is provided by the recent work of Shatzmiller and Lidor[37] involving dianions derived from bis-oxime methyl ethers. The iodine-oxidation product **15** of the dianion **14** produced by dimetalation of **13** suggests that **14** has approximately the ion triplet structure shown.



13 14 15

The ion triplet model helps to rationalize the otherwise remarkable orthometalation of the thiophenolate anion, **16**.[38]



16

Many other examples could be cited to show the application of the same fundamental principles, namely, that free dicarbanions are relatively rare but that the corresponding ion triplets are rather stable and comparatively easy to prepare. In such systems, the dianion charges are best stabilized by being close together rather than far apart. Nevertheless, it should also be emphasized that other factors may be important. For example, in the above examples it was assumed that the dianions involved are the thermodynamically stable systems. In fact, in at least some of these examples the ion triplet structures produced may be the result of kinetic rather than thermodynamic metalation. The distinction may be difficult to establish in individual reactions, particularly for metalations run at low temperature. In any event, our ion-pair acidity determinations are equilibrium processes and the many crystalline dilithio compounds studied also involve minimum-energy structures. Correspondingly, the Coulombic considerations emphasized here should certainly have broad, if not universal, applicability to real reactions.

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