Organic Anions. Part 10.[1] Hard Sphere Electrostatic Calculations on Group 1 Organometallic Compounds

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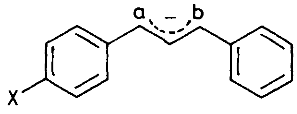
A point charge electrostatic treatment of tetrameric organolithium compounds predicts a quotient of lithium–lithium to carbon–carbon bond lengths of 0.78, which compares with an average experimental value of 0.75. A hard sphere electrostatic (HSE) treatment of hexameric organolithium compounds predicts quotients characterising the shapes and sizes of the carbon and lithium trigonal antiprisms of 1.23, 1.23, and 1.00. The corresponding (average) experimental quotients are 1.13, 1.27, and 0.88. The HSE method is further developed for predicting the structures of group 1 organometallic ion pairs in which a single delocalised anion is associated with several mutually interacting mobile cations. In doing so it is stressed that the critical energy surface (termed the ion-pair surface) is that described by the nucleus of the cation as it rolls over the surface of the anion. The quantitative information obtained from such calculations is crude but it is sufficient to make predictions of a general type. For example a clear division is seen between those anions that will and those that will not form solvent-separated ion pairs. In tetrahydrofuran (THF) all ion pairs R^{2-}, Li^+ will be contact-ion pairs, and most ion pairs of R^{2-}, $2Li^+$ will also be contact-ion pairs but in some *one* of the lithiums may be solvent separated. In triple ions R^-, $2Li^+$, on the other hand, *both* lithiums will be of the solvent-separated type. Calculations on various metal-ion-exchange reactions accord well with experimental findings. In the case of dianions it is predicted that mixing R_1^{2-}, $2M_1^+$ with R_2^{2-}, $2M_2^+$ will sometimes result in an exchange of *both* metal cations but in other cases only *one* will be exchanged. The dominant HSE bonding term for 1:1 ion pairs R^-, M^+ (where R^- is a delocalised anion is that for the atoms immediately in contact with the metal ion and significant delocalisation (in the HSE sense) is that which removes charge from those atoms. Hence in the HSE sense the degree of charge delocalisation in methyl, allyl, and U-pentadienyl anions is the same. The W-conformer of the pentadienyl anion is, however, more charge delocalised and the metal ion is less tightly bound. Throughout this work, HSE calculations are shown to provide a useful first-order guide to the properties of group 1 organometallics.

Electrostatic arguments[2] in organic chemistry have a long history[3] and it is still common for teaching texts to add partial charges to molecules to 'explain' nucleophilic and electrophilic attack. Such 'explanations' must, however, be treated with caution. As Ingold pointed out, organic molecules behave more like Lewis acids and bases than ions or dipoles.[4] This insight has been reinforced by the development of PMO methods[5–10] which allow the energy of interaction between organic molecules to be partitioned and analysed. These show that, except at large separations or in reactions between ions, coulombic factors, although often large,[9] rarely dominate over terms of the charge-transfer type.[5,10] Indeed it is on this fact that the success of FMO theory is based.[11] Hence, although electrostatic arguments are still used for simple nucleophilic, electrophilic,[12] and even pericyclic[13] reactions such arguments may be false.[14] An area where it is probably still valid to use charge-control[7] arguments, however, is that of reactions between ions.[15]

In previous papers in this series[16] we were able to demonstrate that one such ion/ion reaction was charge controlled. It was shown that the relative rate of protonation at site **a** and at site **b** in the perturbed diphenylallyl anion (**1**) could be correlated with the charge difference between these sites as measured by NMR spectroscopy, and that the slope of the correlation line was of the same order of magnitude as that predicted by simple coulombic theory. If the reaction of anion (**1**)[16] (and related anions[15]) with H^+ really is charge controlled, however, it seems reasonable to argue that the same will be true for other reactions with hard[7] acids; for example, group 1 metal ions. In this paper and in the two papers that follow this idea is explored in detail.



(**1**)

In doing so we clearly assume that the dominant bonding interaction in group 1 organometallics is coulombic. This assumption is discussed in greater detail in the next paper but it can be justified *a posteriori*. The simple electrostatic model gives a good guide to both structure and reactivity.

Tetrametric and Hexameric Group 1 Organometallic Aggregates[1]

In ether and hydrocarbon solvents most simple (non-delocalised) group 1 organometallics are aggregated. The commonest aggregation numbers are 2, 4, 6, and 8. The structures of these aggregates are clearly defined and in some cases these persist in the crystalline solid. One of the first of these to be studied by X-ray crystallography was methyl-lithium.[17] This is tetrameric with a tetrahedron of lithium ions surrounded

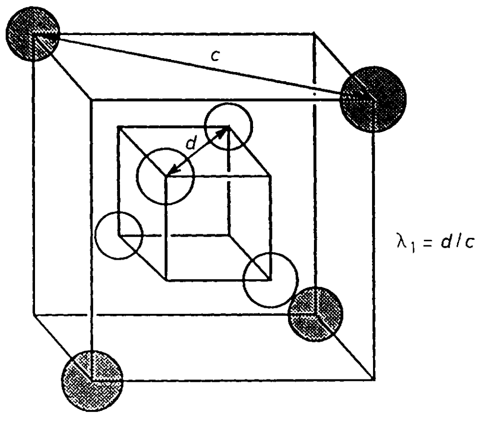


Figure 1.

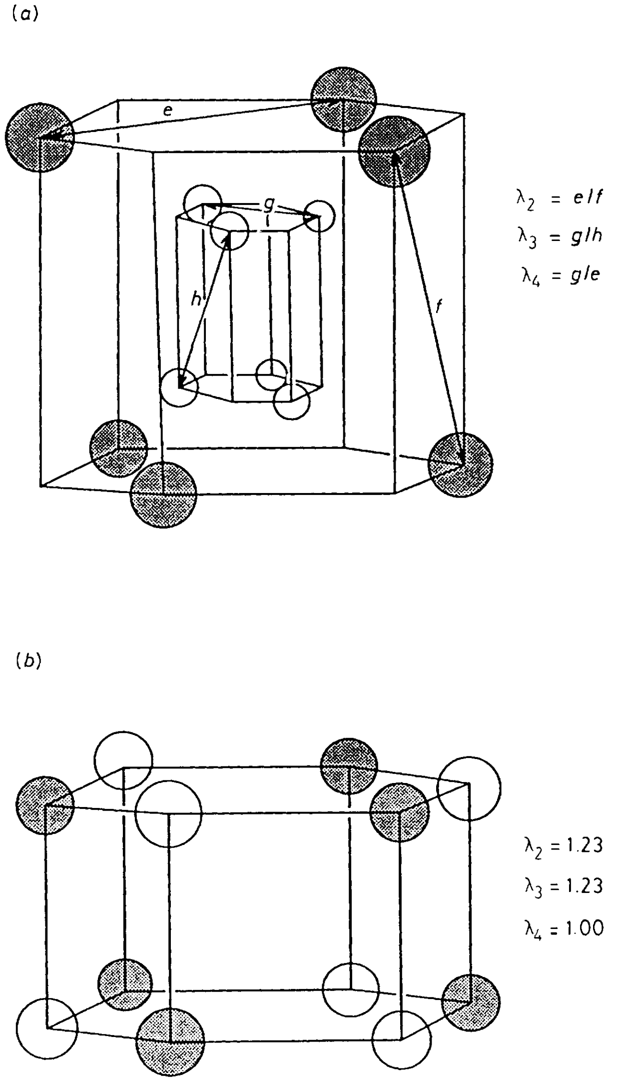


Figure 2.

by a tetrahedron of methyl anions as shown schematically in Figure 1. In one of the earliest applications of simple electrostatics to such systems Streitwieser pointed out that the relative dimensions of this structure can be rationalised using a point-charge model.[18] If we consider that the interaction is purely coulombic (*i.e.*, an equivalent array of positive and negative point charges) then the coulombic energy *E* can be expressed as a function of the C–C bond distance *c* and Li–Li bond distance *d*. It can then be shown that $c{\cdot}E$ is a minimum at λ_1 0.783. In methyl-lithium the λ_1-value is found to be 0.73; remarkably good agreement for such a simple model! However, since it is possible that this agreement is fortuitous[19] we have surveyed a wide range of tetrameric group 1 organometallic compounds.[1] For thirteen such structures we obtained an average value for λ_1 of 0.75 ± 0.07, tending to substantiate Streitwieser's claim.[20]

Since his initial paper on methyl-lithium[18] Streitwieser has used his point charge electrostatic treatment to explain the behaviour of group 1 ion triplets consisting of an organic dianion and two alkali metal cations,[21] and a slightly more elaborate treatment of these has been discussed by Grovenstein.[22] We have also developed a similar treatment of group 1 hexamers.[1] These hexamers can be regarded as having a trigonal antiprism of lithium ions which is surrounded by a trigonal antiprism of anions as shown schematically in Figure 2(*a*). Following the lead given by Streitwieser a relative coulombic energy for this system can be defined in terms of three quotients that define the 'shape' of the cluster. The quotients $\lambda_2 = e/f$ and $\lambda_3 = g/h$ define the shape of the R^- and the Li^+ trigonal antiprisms respectively. Values of $\lambda_2, \lambda_3 < 1.0$ represent a long, thin trigonal antiprism; $\lambda_2, \lambda_3 = 1.0$ represents a regular octahedron; $1.0 < \lambda_2, \lambda_3 < 1.73$ represents a flattened trigonal antiprism; and $\lambda_2, \lambda_3 = 1.73$ represents the limiting case of a flattened trigonal antiprism, a circle of charges. The quotient $\lambda_4 = g/e$ defines the relative sizes of the two trigonal antiprisms. If point charges are used to model such an array, plus and minus charges tend to collapse to a common point and the energy tends towards infinity. When, however, the ions are treated as hard spheres, for most reasonable quotients of the ionic radii (between 0.41 and 1.0), the best solution is $\lambda_2 = \lambda_3 = 1.23$, and $\lambda_4 = 1.0$. This corresponds to a hexagonal prism with square sides as shown in Figure 2(*b*). At the time that our calculations were published in preliminary form[1] only two crystal structures for hexameric organolithiums were available; tetramethylcyclopropylmethyl-lithium[23] and cyclohexyl-lithium.[24] Structures for several other hexameric organolithium compounds have since become available[25–28] and data for these are collected in Table 1. The interatomic distances *e*–*h* (which in cases of structures that were not quite symmetrical have been averaged) were gleaned from the CSSR data base.[29] The basic arrangement of two 'stacked' six-membered rings (λ_2, λ_3, λ_4 = 1.23, 1.23, 1.00) which the HSE model predicts is fairly close to that found in practice and the presence of this arrangement has now been noted by several authors.[26,28]

Delocalised Monomeric Group 1 Organometallic Compounds

1. *The Hard Sphere Electrostatic* (*HSE*) *Model.*—The main concern of this paper and of the two that follow[30,31] is not the HSE treatment of aggregated group 1 organometallics (most of which are derived from 'localised' carbanions) but the HSE treatment of ion pairs of 'delocalised' carbanions. When the degree of charge delocalisation in these anions is sufficiently great they exist in solution as monomeric 'contact' or 'solvent-separated' ion pairs.[32] In many cases, particularly for lithium salts, external solvates of the contact ion pair can be crystallised and in recent years X-ray crystallography has provided unique insights into their structure.[33] The first aim of our work was to show that an HSE model could 'predict' these crystal structures and then to use the model to obtain 'structures' for heavy group 1 metal carbanion salts, for solvent-separated ion pairs, for ion triplets *etc.*; species for which X-ray data are not available and for which it is often difficult to use MO methods. In doing so we

Table 1. A comparison of the relative dimensions of organolithium hexamers (λ_2, λ_3, λ_4; see the text) determined by X-ray crystallography with those predicted by the HSE model.

Compound	λ_2	λ_3	λ_4	Ref.
$[C_6H_{11}Li]_6$	1.13	1.25	0.73	24
$[\text{Tetramethylcyclopropylmethyl-Li}]_6$	1.14	1.21	0.74	23
$[Bu^t_2C{=}NLi]_6$	1.04	1.36	0.91	28
$[Me_2N(C_6H_5)C{=}NLi]$	1.11	1.29	0.89	28
$[(Me_2N)_2C{=}NLi]_6$	1.13	1.29	0.91	28
$[Me_2(\text{naphthyl})SiOLi]_6$	1.16	1.26	0.91	27
$[Bu^t(CH_2{=})COLi]_6$ 1[a]	1.17	1.25	0.95	26
$[Bu^t(CH_2{=})COLi]_6$ 2[a]	1.17	1.25	0.95	26
Average (X-ray)	1.13	1.27	0.88	
HSE prediction	1.23	1.23	1.00	

[a] Two slightly different hexamers per unit cell. To two decimal places, however, λ_2, λ_3, and λ_4 are the same.

have also obtained semiquantitative estimates of the electrostatic component of the bonding energies. We have correlated these with literature data on ion pair equilibria and used them to make predictions concerning such equilibria.

The model for these calculations has been kept as simple as possible,[34] basing it on that which has been used for many years to explain the relative stabilities of extended ionic inorganic crystal lattices; (for example, the effect of ionic radii on the relative stabilities of the sodium chloride, caesium chloride, and zinc blende structures).[35] The main assumptions made are (1) that the organic anion is composed of hard sphere atoms whose positions are fixed in space; (2) that the charge on each atom can be approximated as a point charge located at its nucleus; (3) that the solvated cation can be treated as a freely moving hard sphere with unit positive charge; (4) that except for hard sphere/hard sphere volume exclusion interactions the only interaction between the organic anion and the solvated cation is electrostatic; (5) that the minimum energy for the system is found when the anion and cation are in contact; (6) that the medium behaves as a continuous dielectric whose dielectric constant (relative permitivity) ε is independent of the anion/cation separation; (7) that polarisation of the nuclear positions[36] and of the charge distribution[12,13,37] can be ignored; and (8) that specific effects of solvent can be ignored.

Clearly it would have been possible to use a more sophisticated charge-distribution function,[2,12,13] or a more sophisticated definition of the anion surface,[12,13] or to allow for charge polarisation* but since neither the effect of a non-uniform dielectric nor the effect of solvent can be treated exactly, and since treatment of polarisation of nuclear positions is difficult, a rigorous quantitative calculation is out of the question. Under these circumstances the simplest model seems to be the best. Within the assumptions of this model the main parameters that have to be considered are the atomic/ionic radii, the charges, the anion geometries, and the dielectric constant. The only other problem to be overcome is that of searching the relevant energy surface.

(i) *The choice of hard sphere atomic and ionic radii.* Throughout this work van der Waals radii have been used for carbon and hydrogen (C = 1.70; H = 1.20 Å)[38] and the radius for (externally solvated) Li^+ was fixed at 0.57 Å to match the average C–Li distance as determined by X-ray crystallography for a series of organolithium crystal structures.[34] This is very close to Pauling's value of 0.60 Å.[39] Pauling's radii have been used for the remaining group 1 metal ions[39] and a value of 4.50 Å was chosen for the fully solvated lithium ion to fit that determined empirically for Li^+ solvent-separated ion pairs in THF.[32] In fact slight variations in these values do not change either the predicted structures of the ion pairs or the general trends in energies. It should also be noted that it is the sum of the radii and not the way in which they are partitioned that determines the three-dimensional form of the ion-pair surface (in this case r_{CLi} 2.27; r_{HLi} 1.78; r_{CCs} 3.39; r_{HCs} 2.28; r_{CSS}† 6.2; r_{HSS}† 5.7 Å)

(ii) *The choice of charge distribution.* Although it is conceptually simple, the use of atomic charges to represent the charge distribution creates a problem since such charges, derived from a Mulliken population analysis of the MO wavefunction, are notoriously dependent on the MO method and the basis set employed. We have tested the effect of using charges derived from various MO methods (HMO, CNDO-II, and *ab initio* STO-3G) on our calculations. For most of the systems we have studied the use of CNDO-II and *ab initio* STO-3G charge distributions gives more high-energy local energy minima and a flatter energy surface than the use of HMO charges, but so far as the ordering of the major energy minima is concerned the differences are not too significant.[30,31] In comparing trends in bonding energies from one system to the next, provided that one self-consistent set of results is used, conclusions are unaffected.

(iii) *The choice of anion geometries.* As far as possible the anion geometries used as a basis for the MO calculations and for the HSE calculations were derived from X-ray crystallographic data[29] although in a few cases geometries optimised by MO methods were employed.[30,31]

(iv) *The choice of dielectric constant.* The problem of how to treat the dielectric constant (relative permittivity) ε at the molecular level is one to which there is no universally accepted solution. *a priori* it seems reasonable to argue that for two well separated ions the value for the bulk solvent should apply but as the separation between the ions decreases so should the dielectric constant, perhaps approaching a limiting value of 1.0 when the ions are in contact and there are no intervening solvent molecules. Such models where the dielectric constant is a function of distance have been proposed[40,41] but have not been widely adopted. Most often authors have assumed that the effective microscopic dielectric constant is independent of distance but is somewhat less than that of the bulk solvent.[38,41] This has advantages for the present calculations since ε can then be factored out. In a continuous medium the electrostatic bonding energy between a point charge cation (charge +1) and a point charge anion (charge $-z_i$) at a separation r_i is given in equation (1) where e is the electronic charge. If the anion is made

$$E = \frac{e^2}{\varepsilon} \cdot \frac{z_i}{r_i} \qquad (1)$$

up of an array of point charges the electrostatic interactions must be summed [equation (2)]

$$E = \Sigma_i \frac{e^2}{\varepsilon} \cdot \frac{z_i}{r_i} \qquad (2)$$

Provided ε is not a function of r (*i.e.*, we assume a constant reduced relative permittivity) and r is not a function of ε (which is true for the HSE model but not, for example, in models where the hard sphere repulsive potential is replaced by a Lennard Jones potential[42]) equation (2) can be rewritten as equation (3).

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* The errors introduced by ignoring polarisation of the charge distribution have been discussed by Hehre and co-workers (refs. 12 and 13).

† Throughout these papers SS^+ is used as an abbreviation for the fully solvated counter-ion in solvent-separated ion pairs and is modelled on Li^+, 4 THF.

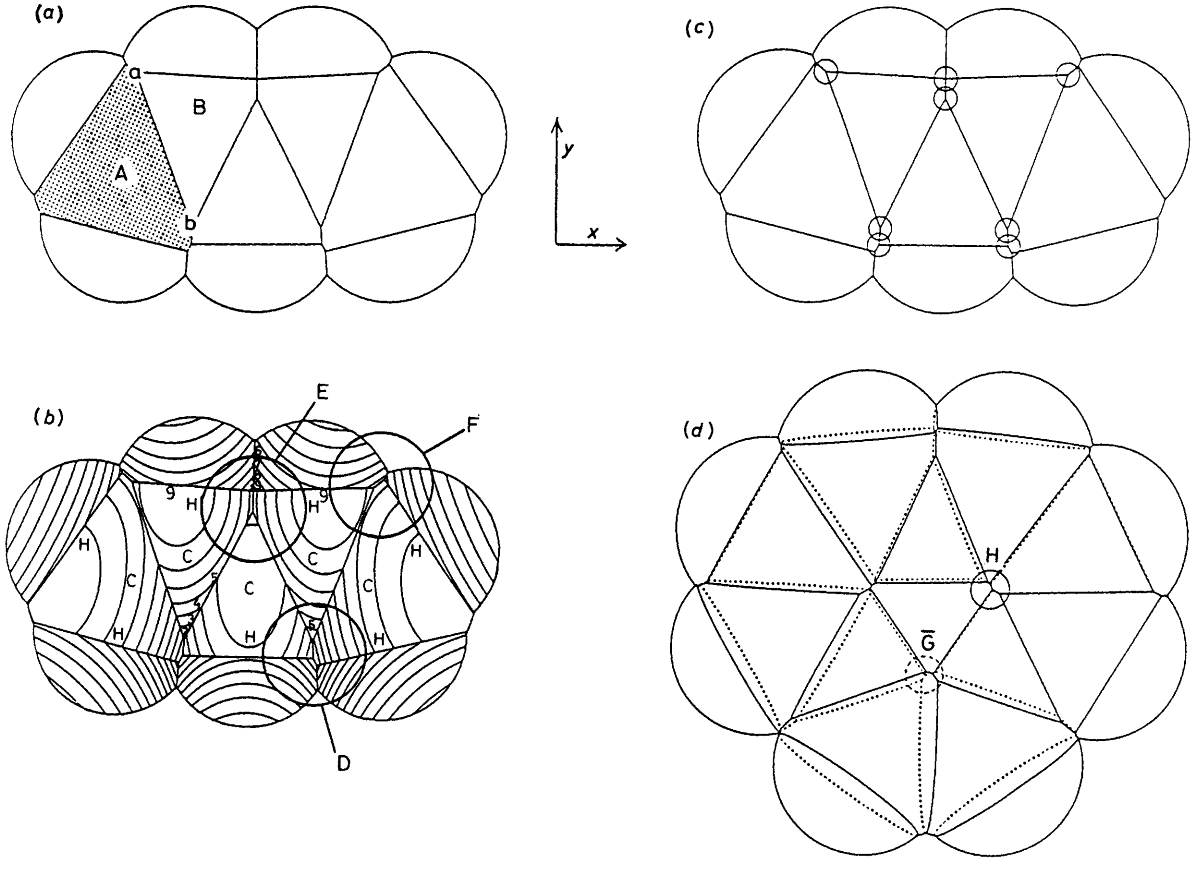

Figure 3.

$$E\cdot\varepsilon = e^2\Sigma_i \frac{z_i}{r_i} \qquad (3)$$

The energy surface is then expressed in terms of $E\cdot\varepsilon$ which has normal energy units but is independent of the medium and of the value of ε.

(v) *Search for and display of energy surfaces.* There are several well established methods for calculating and displaying electrostatic potentials around a molecule.[2,12,13,37,43–45] Unfortunately these are of no use in predicting the structures of ion pairs where there are several mobile counterions and are of little use even for the simple case where there is only one mobile counterion. The commonest approach is to display the potential in a plane taken through the molecule or, in the case of planar anions, a plane above and parallel to that of the molecule itself.[37,44] Unfortunately, to locate the relevant minimum for a cation a very large number of these planes must be examined visually and, unless those regions within these planes excluded to the cation on steric grounds are also shown,[43] incorrect predictions can easily result.[34,44] For ion pairing problems potentials at distances shorter or longer than those allowed by atom–atom contacts are not actually required and only confuse the picture. The actual surface of interest (hereinafter referred to as the ion-pair surface) is that described by the nucleus of the counterion as it is rolled over the surface of the anion.[12,13,45] In the hard sphere model this looks very much like an expanded van der Waals surface and an example (for the Li^+ salt of the W-conformer of the pentadienyl anion) is shown in Figure 3(*a*). It must, however, be remembered that this is *not* a van der Waals surface but *a surface representing potential positions of the nuclei of the cation.* On this surface, areas such as the shaded area **A** represent η^1 sites; in this case sites in which Li^+ contacts only C-1. An internal line such as the line between **a** and **b** represents η^2 sites; in this case sites where Li^+ bridges C-1 and C-2. A point such as point **b** represents an η^3 site (or in general an η^3, η^4, η^5, *etc.*, site) in this case one where Li^+ bridges between C-1, C-2, and C-3.

The best method of searching for energy minima on this surface is not immediately obvious. The simplest approach for a planar anion and a single counterion is to calculate energies at points on this surface using a regular grid in x and y and to use a standard contour-fitting routine to produce diagrams such as Figure 3(*b*). From this it is clear that the major minimum is close to the circled region **D** with possible local minima in the circled regions **E** and **F**. Does, however, region **D** contain one, two, or three local minima, and in region **F** are there two, one, or none at all? For simple molecules like this one these questions can be answered by expanding the view of each region in turn and producing a new contour map based on a very fine grid of points. For large molecules, however, this becomes a very slow process and the approach cannot be generalised to the case of several mobile counterions. An automated search procedure was therefore developed. The first versions of this were based on an atom-by-atom search.[34] Referring to Figure 3(*a*) all points on the surface **A** can be generated simply by using equations (4)–(6).

$$x = x_1 + r_{1j}\cdot\sin\theta \qquad 0 < \theta < 2\pi \qquad (4)$$
$$0 < \varphi < \pi$$

$$y = y_1 + r_{1j}\cdot\cos\theta\cos\varphi \qquad r_{1j}\ 2.27\ \text{Å} \qquad (5)$$

$$x = x_1 + r_{1j}\cdot\cos\theta\sin\varphi \qquad x_1 = x \text{ co-ordinate of C-1, } etc. \qquad (6)$$

This surface can then be searched either by a grid method[34] (allowing for the fact that some regions are inaccessible by virtue of atom/atom contacts), or, from a number of start points θ_i, φ_i a standard routine can be used to minimise the energy as a function of θ and φ.[46] The problem with such a method is that minima invariably occur at η^2, η^3, *etc.*, sites and to check that a point (say **b**) is a true minimum it is necessary to transfer from a co-ordinate system based on C-1 to one based on C-2 and then C-3 and check that **b** is a minimum in all three co-ordinate systems! Such a program has been developed but the method is cumbersome and difficult to adapt for several mobile counterions. A more satisfactory solution for planar molecules is to use a series of start points in the x/y plane and to search $E{\cdot}\varepsilon$ on (say) the upper ion-pair surface as a function of x and y (for any given x and y the z co-ordinate of either upper or lower surface is easy to calculate). This approach can be generalised to the case of N mobile counterions when $E{\cdot}\varepsilon$ becomes a function of N pairs of variables x_1, y_1, x_2, y_2; $\cdots\cdots x_N$, y_N although cation/cation repulsions must be included, and cases where there are different distributions of cations between the top and bottom surfaces have to be treated separately. The problem in implementing this approach is that most computer routines for minimising a function of several variables only work well for a continuous function, and each line in Figure 3(*a*) represents a discontinuity in $E{\cdot}\varepsilon$ as a function of x and y. The practical result is that such routines often find spurious 'minima' on the edge of the molecule, or for example, at a point in the middle of line *a,b*. In the programs that we have written this problem is overcome first by choice of the right energy-minimisation routine,* secondly by rejecting all apparent 'minima' on the edge of the molecule, and finally by using all other apparent 'minima' as start points for a reminimisation routine and only accepting those that consistently give the same solution. In this way programs have been written that automatically and reliably locate all local energy minima on the ion-pair surface. Typical examples of the graphical output from these programs are given in Figures 3(*c*) and 3(*d*). Figure 3(*c*) shows the output where energy minima for a single Li^+ counterion paired with the W-conformation of the pentadienyl anion have been located. Each one is indicated by a small circle. In such calculations we find that about 20 × (number of carbon atoms) start points are required to locate *all* of the local minima. Figure 3(*d*) shows typical graphical output for a *two* counterion problem; in this case the dilithium salt of the acenaphthalene dianion. Since this dianion is not quite planar the upper and lower ion-pair surfaces are inequivalent and data for the lower surfaces are encoded by the use of dashed lines. In this case one set of output is produced for each local minimum, and separate searches are required to locate the minima with one lithium on the top and one on the bottom, for minima with both lithiums on the top, and for minima with both lithiums on the bottom. The minimum represented has one lithium above one of the six-membered rings and one below the five-membered ring. In all of the cases reported in this and the following papers all local minima discovered by the automated searches were carefully checked by visual inspection of a suitably magnified contour plot. In the two-cation case two such plots must be produced for each local minimum. For example, in the case illustrated in Figure 3(*d*) a contour plot for the lower surface in the region of $\bar{\mathbf{G}}$ for the field of the dianion plus that of a cation at **H** must be produced and then one for the upper surface in the region of $\underline{\mathbf{H}}$ for the dianion plus a cation at $\bar{\mathbf{G}}$. Such a visual check of the ion-pair surface is essential.

2. *HSE Bonding Energies.*—The main aim in developing the HSE method for delocalised organic anions was to see if it could predict the structures of contact-ion pairs and in this respect it works quite well.[30,31] Because the method involves gross approximations it was not expected to provide useful quantitative information, but when all of the bonding energy data are collected together interesting general trends emerge. These trends seem to be significant and it is these that will be discussed in the rest of this paper.

Table 2 summarises the HSE bonding energies $E{\cdot}\varepsilon$ for all of the anions we have studied. All of the data refer to HMO charge distributions; $E(Li^+)\varepsilon$ refers to one lithium counterion; $E(2Li^+)\varepsilon$ refers to two lithium counterions, *etc.* (C^-) refers to a hypothetical spherical anion with unit negative charge and the same atomic radius as carbon. The entries in this Table have been ranked in order of decreasing bonding energy towards a single lithium ion [$E(Li^+)\varepsilon$] and this same rank order has also been used in Tables 3–6. It should be noted that the rank order for $E(Li^+)\varepsilon$ is very similar to that for $E(Cs^+)\varepsilon$ and for $E(SS^+)\varepsilon$, the bonding energies merely decreasing with increasing size of the counterion. More significant irregularities in rank order are seen for the cases where there are two counterions, particularly $E(2Li^+)\varepsilon$. This is because the cation–cation repulsion is very dependent on the size and shape of the anion and it is particularly significant for the dilithium salts.

The 'rank order' of ions in Table 2 conforms more or less to that which would be expected purely on qualitative grounds. Dianions rank higher than monoanions and more 'localised' ions rank higher than 'delocalised' ions. It should, however, be noted that significant delocalisation in the HSE sense is a little different from charge delocalisation as it is normally understood. Significant charge delocalisation in the HSE sense is that which *removes charge from the carbons immediately in contact with the cation.* In the HSE model, for a 1:1 ion pair, R^-, M^+, provided that the cation is in contact with all of the charge-bearing carbons, the bonding energy is independent of how that charge is divided up. Hence $E(M^+)\varepsilon$ is almost the same for (C^-) (one carbon of unit negative charge), for allyl$^-$ (two carbons each charge $-\frac{1}{2}$),[30] for U-pentadienyl$^-$ (three carbons each charge $-\frac{1}{3}$),[30] for cyclopentadienyl$^-$ (five carbons each charge $-\frac{1}{5}$),[30] and for benzene$^{\cdot-}$ (six carbons each charge $-\frac{1}{6}$),[31] and is half of the value for benzene^{2-} (six carbons each charge $-\frac{1}{3}$).[31] Small differences from strict equality arise because 'real' rather than idealised geometries have been used so that in cyclopentadienyl$^-$ for example, it is not quite possible for the Li^+ to contact all five carbons at once. It is clear that, whilst in the normal sense the degree of the charge delocalisation in these ion pairs varies, in the HSE sense they are equivalent. Conversely, situations arise where in the normal sense the charge delocalisation is the same, but in an HSE sense there are important differences. For example the U and W conformers of pentadienyl$^-$ (Table 2, entries 12 and 17). In the U-conformer the carbon bridges all three charge-bearing carbons but in the W-conformer only two.[30] This has significant chemical consequences, for example in contact/solvent-separated ion-pair equilibria.

3. *Solvent-separated/Contact-Ion Pair Equilibria.*—The conversion of a contact-ion pair into a solvent-separated ion pair[32] involves an increase in the separation between the ions and hence a decrease in the electrostatic bonding energy. For

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* These programs were based around the NAGF Mark II library routine EO4JAF which finds a minimum of a function of several variables subject to fixed bounds on the variables and which employs a quasi-Newtonian method. It is intended for continuous functions with continuous first and second derivatives but will also cope with some discontinuities. Details of the implementation of our method and the programs written are given in the Ph.D. Thesis of H. L. Steel, University of Leeds, 1989.

Table 2. HSE ion-pair bonding energies based on HMO charge distributions.[a]

	$E(\mathrm{Li}^+)\varepsilon$	$E(2\mathrm{Li})\varepsilon$	$E(\mathrm{Cs}^+)\varepsilon$	$E(2\mathrm{Cs}^+)\varepsilon$	$E(\mathrm{SS}^+)\varepsilon$	$E(2\mathrm{SS}^+)\varepsilon$	$E(\mathrm{Li}^+\mathrm{Cs}^+)\varepsilon$	$E(\mathrm{Li}^+\mathrm{SS}^+)\varepsilon$	Δ_1	Δ_2	Δ_3
1 Benzene^{2-}	−292.1	−491.7	−195.7	−337.8	−107.1	−186.7	−419.9	−356.8	185.0	134.9	170.1
2 Naphthalene^{2-}	−237.1	−397.0	−173.2	−296.2	−102.4	−177.8	−349.1	−298.9	134.7	98.1	121.1
3 Phenanthrene^{2-}	−234.0	−374.7	−171.4	−288.9	−101.9	−176.1	−337.2	−293.4	132.1	81.3	117.3
4 Acenaphthalene^{2-}	−232.5	−381.2	−170.7	−289.3	−101.8	−176.3	−339.9	−293.7	130.7	87.5	117.4
5 Anthracene^{2-}	−227.8	−364.0	−169.0	−282.5	−101.5	−173.9	−327.6	−285.7	126.3	78.3	111.8
6 (*E*)-Stilbene^{2-}	−224.1	−370.8	−164.8	−279.4	−99.5	−172.1	−327.7	−283.1	124.6	87.7	111.0
7 (*Z,E,Z*)-Hexatriene^{2-}	−196.8	−314.5	−138.5	−225.8	−80.3	−133.7	−274.0	−236.3	116.5	78.2	102.6
8 (C$^-$)	−146.3	−219.4	−98.0	−146.9	−53.6	−80.3	−185.6	−160.6	92.7	58.8	80.3
9 Allyl$^-$	−146.3	−193.8	−98.0	−139.4	−53.6	−79.3	−173.5	−156.9	92.7	36.9	77.6
10 Cyclopentadienyl$^-$	−146.1	−206.7	−97.9	−143.6	−53.5	−79.8	−179.2	−158.4	92.6	48.3	78.6
11 Benzene$^{-\bullet}$	−146.1		−97.8		−53.5				92.6		
12 U-Pentadienyl$^-$	−145.7	−181.0	−97.8	−138.5	−53.5	−79.2	−167.8	−154.5	92.2	26.5	75.3
13 Indenyl$^-$	−135.8	−185.8	−93.5	−134.8	−52.6	−77.9	−164.4	−147.1	83.2	38.7	69.2
14 Benzyl$^-$	−130.4	−182.8	−91.5	−131.8	−52.3	−77.0	−160.1	−141.8	78.1	41.0	64.8
15 S-Pentadienyl$^-$	−129.9	−175.3	−91.5	−128.3	−52.3	−76.8	−155.7	−140.1	77.6	35.2	63.3
16 Fluorenyl$^-$	−127.0	−167.6	−89.8	−127.2	−51.8	−76.2	−151.6	−137.3	75.2	30.3	61.1
17 W-Pentadienyl$^-$	−123.0	−166.9	−87.3	−123.3	−51.1	−75.2	−149.1	−133.9	71.9	33.0	58.7
18 Benzhydryl$^-$	−122.2	−158.0	−87.4	−120.0	−51.2	−74.6	−143.3	−131.2	71.0	26.8	56.6
19 (*Z,Z*)-1,3-Diphenylallyl$^-$	−118.9	−152.6	−84.8	−118.8	−49.8	−72.7	−140.2	−128.0	69.1	24.6	79.9
20 Naphthalene$^{-\bullet}$	−118.6		−86.6		−51.2				67.4		
21 (*E,Z*)-1,3-Diphenylallyl$^-$	−118.5	−148.6	−85.4	−114.9	−50.4	−73.0	−136.5	−126.3	68.1	22.3	53.3
22 Phenanthrene$^{-\bullet}$	−117.0		−85.7		−51.0				66.0		
23 Anthracene$^{-\bullet}$	−113.9		−84.5		−50.8				63.1		
24 (*E,E*)-1,3-Diphenylallyl$^-$	−113.8	−145.0	−82.4	−112.5	−49.5	−71.7	−132.5	−123.0	64.3	22.0	51.3
25 (*E*)-Stilbene$^{-\bullet}$	−112.1		−82.4		−49.8				62.3		
26 Trityl$^-$	−111.8	−145.3	−83.4	−114.7	−49.0	−71.4	−133.0	−121.0	62.8	24.3	49.6
27 (*Z,E,Z*)-Hexatriene$^{-\bullet}$	−98.4		−69.3		−40.2				58.2		

[a] $E(\mathrm{Li}^+)\varepsilon$ is the ion pair bonding energy for one Li$^+$ counter ion (kcal mol^{-1}); (C$^-$) represents a sphere of unit charge and the same radius as carbon. Δ_1 *etc.* defined in the text.

Table 3. HSE calculated energies for the reaction $R_1Li + R_2Cs \longrightarrow R_1Cs + R_2Li$. A negative value indicates that reaction will proceed in the direction indicated.

	R_1									
R_2	8 (C)$^-$	9 Allyl$^-$	10 Cyclopentadienyl$^-$	13 Indenyl$^-$	14 Benzyl$^-$	16 Fluorenyl$^-$	17 W-Pentadienyl$^-$	18 Benzhydryl$^-$	24 (*E,E*)-Diphenylallyl$^-$	26 Trityl$^-$
8 (C)$^-$	0.0	0.0	−0.1	−6.0	−9.4	−11.1	−12.6	−13.5	−16.9	−19.9
9 Allyl$^-$	0.0	0.0	0.0	−6.0	−9.4	−11.1	−12.6	−13.5	−16.9	−19.9
10 Cyclopentadienyl$^-$	0.1	0.1	0.0	−5.9	−9.3	−11.0	−12.5	−13.4	−16.8	−19.8
13 Indenyl$^-$	6.0	6.0	5.9	0.0	−3.4	−5.1	−6.6	−7.5	−10.9	−13.9
14 Benzyl$^-$	9.4	9.4	9.3	3.4	0.0	−1.7	−3.2	−4.1	−7.5	−10.5
16 Fluorenyl$^-$	11.1	11.1	11.0	5.1	1.7	0.0	−1.5	−2.4	−5.8	−8.8
17 W-Pentadienyl$^-$	12.6	12.6	12.5	6.6	3.2	1.5	0.0	−0.9	−4.3	−7.3
18 Benzhydryl$^-$	13.5	13.5	13.4	7.5	4.1	2.4	0.9	0.0	−3.4	−6.4
24 (*E,E*)-Diphenylallyl$^-$	16.9	16.9	16.8	10.9	7.5	5.8	4.3	3.4	0.0	−3.0
26 Trityl$^-$	19.9	19.9	19.8	13.9	10.5	8.8	7.3	6.4	3.0	0.0

Table 4. HSE calculated energies for the reaction $R_1{}^{2-}, 2Li^+ + R_2{}^{2-}, 2Cs^+ \longrightarrow R_1{}^{2-}, 2Cs^+ + R_2{}^{2-}, 2Li^+$. A negative value indicates an HSE driving force for the reaction in the direction shown.

	R_1							
R_2	(C)$^{2-}$	Benzene^{2-}	Naphthalene^{2-}	Phenanthrene^{2-}	Acenaphthalene^{2-}	Anthracene^{2-}	Stilbene^{2-}	Hexatriene^{2-}
(C)$^{2-}$	0.0	−15.3	−68.4	−83.4	−77.3	−87.7	−77.8	−80.5
1 Benzene^{2-}	15.3	0.0	−53.1	−68.1	−62.0	−72.4	−62.5	−65.2
2 Naphthalene^{2-}	68.4	53.1	0.0	−15.0	−8.9	−19.3	−9.4	−12.1
3 Phenanthrene^{2-}	83.4	68.1	15.0	0.0	6.1	−4.3	5.6	2.9
4 Acenaphthalene^{2-}	77.3	62.0	8.9	−6.1	0.0	−10.4	−0.5	−3.2
5 Anthracene^{2-}	87.7	72.4	19.3	4.3	10.4	0.0	9.9	7.2
6 Stilbene^{2-}	77.8	62.5	9.4	−5.6	0.5	−9.9	0.0	−2.7
7 Hexatriene^{2-}	80.5	65.2	12.1	−2.9	3.2	−7.2	2.7	0.0

Table 5. HSE calculated energies for the reaction $R_1{}^{2-}, 2Li + R_2{}^{2-}, 2CS^+ \longrightarrow R_1{}^{2-}, Li^+, Cs^+ + R_2{}^{2-}, Li^+, Cs^+$. A negative value indicates that the reaction would proceed in the direction shown.

	R_1							
R_2	$(C)^{2-}$	Benzene^{2-}	Naphthalene^{2-}	Phenanthrene^{2-}	Acenaphthalene^{2-}	Anthracene^{2-}	Stilbene^{2-}	Hexatriene^{2-}
$(C)^{2-}$	−4.8	−15.2	−39.1	−49.5	−45.7	−50.6	−43.9	−46.5
1 Benzene^{2-}	0.1	−10.3	−34.2	−44.6	−40.8	−45.7	−39.0	−41.6
2 Naphthalene^{2-}	29.3	18.9	−5.0	−15.4	−11.6	−16.5	−9.8	−12.4
3 Phenanthrene^{2-}	33.9	23.5	−0.4	−10.8	−7.0	−11.9	−5.2	−7.8
4 Acenaphthalene^{2-}	31.6	21.2	−2.7	−13.1	−9.3	−14.2	−7.5	−10.1
5 Anthracene^{2-}	37.1	26.7	2.8	−7.6	−3.8	−8.7	−2.0	−4.6
6 Stilbene^{2-}	33.9	23.5	−0.4	−10.8	−7.0	−11.9	−5.2	−7.8
7 Hexatriene^{2-}	34.0	23.6	−0.3	−10.7	−6.9	−11.8	−5.1	−7.7

Table 6. HSE predictions for the mixing of $R_1{}^{2-}, 2Li^+$ and $R_2{}^{2-}, 2CS^+$.[a]

	R_1							
R_2	$(C)^{2-}$	Benzene^{2-}	Naphthalene^{2-}	Phenanthrene^{2-}	Acenaphthalene^{2-}	Anthracene^{2-}	Stilbene^{2-}	Hexatriene^{2-}
$(C)^{2-}$	M	T	T	T	T	T	T	T
1 Benzene^{2-}	N	M	T	T	T	T	T	T
2 Naphthalene^{2-}	N	N	M	M	M	T	M	M
3 Phenanthrene^{2-}	N	N	M	M	M	M	M	M
4 Acenaphthalene^{2-}	N	N	M	M	M	M	M	M
5 Anthracene^{2-}	N	N	N	M	M	M	M	M
6 Stilbene^{2-}	N	N	M	M	M	M	M	M
7 Hexatriene^{2-}	N	N	M	M	M	M	M	M

[a] N = no exchange; M = exchange giving the mixed salts $R_1{}^{2-}, Li^+, Cs^+$ and $R_2{}^{2-}, Li^+Cs^+$; T = exchange of both cations giving $R_1{}^{2-}, 2Cs^+$ and $R_2{}^{2-}, 2Li^+$.

lithium salts HSE estimates of this loss can be gleaned from Table 2, in which the terms $\Delta_1, \Delta_2, \Delta_3$ refer to the reactions (7)–(9).

$$R^{n-}, Li^+ \longrightarrow R^{n-}, SS^+ \qquad \Delta_1 = E(SS^+)\varepsilon - E(Li^+)\varepsilon \qquad (7)$$

$$R^{n-}, 2Li^+ \longrightarrow R^{n-}, Li^+, SS^+ \qquad \Delta_2 = E(Li^+, SS^+)\varepsilon - E(2Li^+)\varepsilon \qquad (8)$$

$$R^{n-}, Li^+, SS^+ \longrightarrow R^{n-}, 2SS^+ \qquad \Delta_3 = E(2SS^+)\varepsilon - E(Li^+, SS^+)\varepsilon \qquad (9)$$

The loss in electrostatic bonding energy in going from contact to solvent-separated ion pair is partly balanced by a gain in solvation energy. This solvation energy is a function mainly of the nature of the cation and of the solvent and in the simplest model it can be assumed to be constant for a given cation/solvent combination. Even with this assumption, however, it is not easy to compare the results of HSE calculations with experimental results since these are widely scattered through the literature and are of very variable quality. In Figures 4 and 5, however, such comparisons are made. In these Figures values of Δ_1 taken from Table 2 are plotted along the horizontal axis and the lengths of the shaded bars represent measured percentages of solvent-separated ion pairs in THF at room temperature for lithium[47–60] and sodium salts[47,48,52,54,58–64] respectively. In some cases these percentages have been averaged from several literature values.

Figures 4 and 5 show the expected dependence of the contact-ion pair/solvent-separated ion pair equilibrium on counterion, formation of solvent-separated ion pairs being more favoured for lithium than sodium salts. There is also a general correlation with Δ_1-values. The changeover from one type of ion pair to the other type for lithium salts in THF at 25 °C occurs at roughly Δ_1 75 kcal mol^{-1}. Above Δ_1 85 kcal mol^{-1} only contact-ion pairs are formed and below Δ_1 65 kcal mol^{-1} only solvent-separated ion pairs. Use of these data in conjunction with Table 2 allows some interesting predictions to be made. For example, it is clear that, for THF solutions at room temperature, monolithium salts of dianions will form only contact-ion pairs, R^{2-}, Li^+, (Table 2, values of Δ_1 for entries 1–7 are all >116.5 kcal mol^{-1}) and for some monoanion monolithium salts R^-, Li^+ (for which there are no experimental data) clear predictions can be made: contact-ion pairs for benzene$^{-\bullet}$ Li^+; solvent-separated ion pairs for anthracene$^{-\bullet}$, Li^+; stilbene$^{-\bullet}$, Li^+; and hexatriene$^{-\bullet}$, Li^+. The diagram also serves to emphasise the point made previously that charge delocalisation in the HSE sense is rather different from that in the normally accepted sense. Hence, using the example of pentadienyl lithium, the W-conformer is more delocalised (in the HSE sense) than is the U-conformer. This provides the 'theoretical' basis for the observation that W-conformers may give solvent-separated ion pairs whereas the U-conformers always give contact-ion pairs.[53] Use of values of Δ_2 and Δ_3 from Table 2 allows predictions to be made for dilithium salts. For most dianion dilithium salts bis-contact ion pairs, $R^{2-}, 2Li^+$, will predominate. It has often been assumed that these are the only sorts of ion pairs formed by dianions.[65] The data given in Table 2, however, suggest that mono-contact, mono-solvent-separated ion pairs, R^{2-}, Li^+, SS^+, could form (entries 1–7) in some cases and there is experimental evidence to suggest that this is true.[58,66] For ion triplets of monoanions, on the other hand, it is clear that bis-contact ion pairs, $R^-, 2Li^+$,

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* 1 cal = 4.185 J.

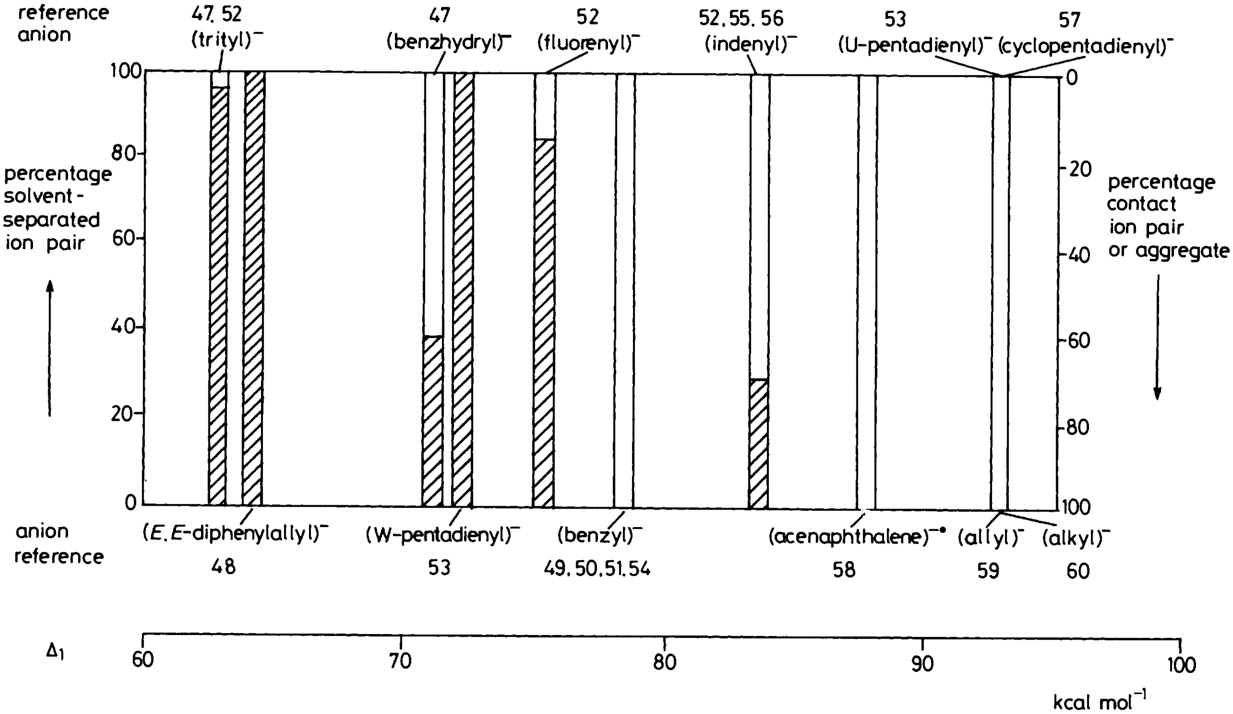

Figure 4.

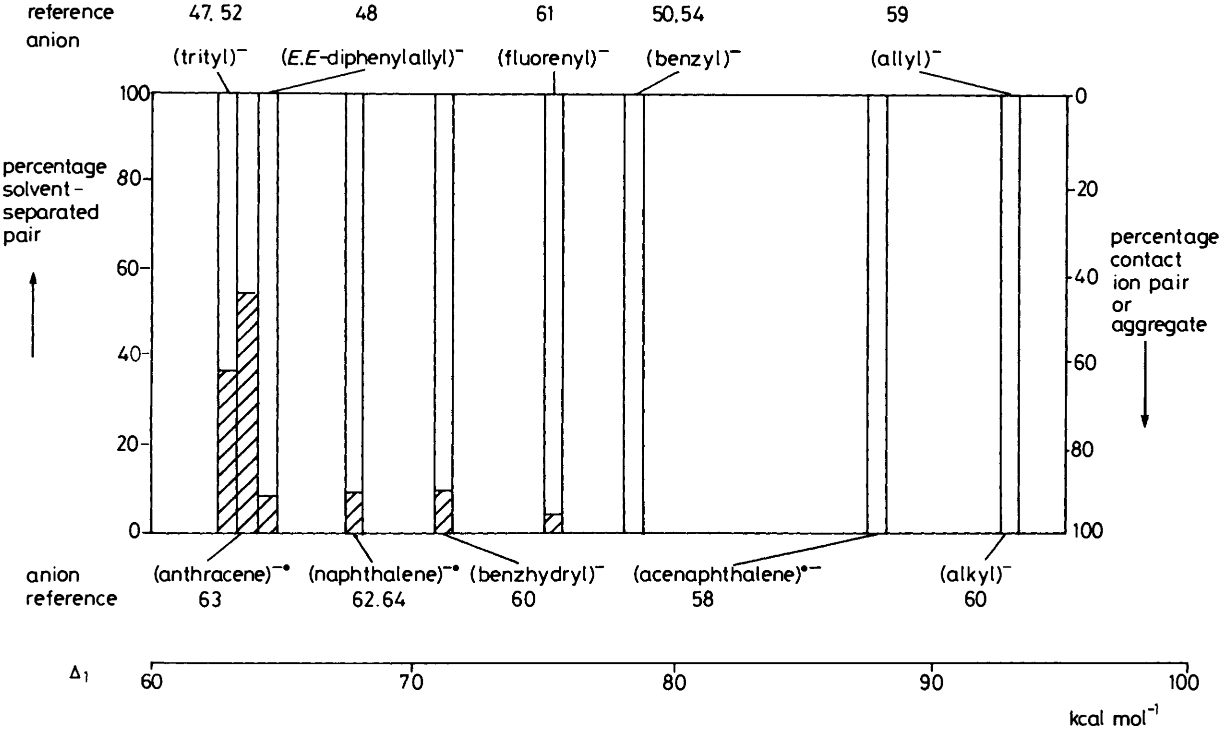

Figure 5.

are highly unlikely in THF at room temperature (Table 2, values of Δ_2 entries 8–26 are all <60 kcal mol^{-1}) and although for a few localised ions ion pairs of the type R^-, Li^+, SS^+ may form, in most cases bis-solvent-separated ion pairs, $R^-, 2SS^+$, will predominate (Table 2, values of Δ_3 entries 8–26).

4. *Triple Ion Formation.*[67]—The simplest reaction in which a triple ion is formed is given by equation (10).* If we assume

$$2R_1^-, M^+ \longrightarrow R_1^-, 2M^+ + R_1^- \qquad (10)$$

that this reaction occurs without a change in ion-pair type and that the solution is infinitely dilute so that R_1^-, $2M^+$ and R_1^- do not interact, an HSE estimate of the change in coulombic

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* Here and throughout, subscript 1,2 indicate different R groups, *not* multiplying factors [*cf.* and contrast equation (15)].

bonding energy can be made using the data in Table 2 {$\Delta = E(2\mathrm{M}^+)\varepsilon - 2[E(\mathrm{M}^+)\varepsilon]$}. The process is always unfavourable. The energy cost is only weakly dependent on the structure of R_1^- but it decreases markedly in going from Li^+ to Cs^+ to SS^+ ion pairs. A slightly more complex example of triple ion formation is that where two organometallics are mixed [equation (11)]. The change in HSE bonding energy for this reaction can also be calculated from the data in Table 2. Although there are some irregularities in order, the sense in which the reaction occurs is normally that where the anion R_1^- is ranked above R_2^- in Table 2; *i.e.*, the anion which is more strongly bonding, more localised in the HSE sense, is the one which forms the triple ion. Also, although for the anions listed in Table 2 the process is always unfavourable, the energy cost for triple ion formation generally becomes smaller the greater the separation between R_1^- and R_2^- in Table 2.[68]

$$\mathrm{R}_1^-,\mathrm{M}^+ + \mathrm{R}_2^+,\mathrm{M}^+ \longrightarrow \mathrm{R}_1^-,2\mathrm{M}^+ + \mathrm{R}_2^- \quad (11)$$

5. *Cation-exchange Reactions.*—The simplest $\mathrm{Li}^+/\mathrm{Cs}^+$ exchange reactions can be represented by equation (12). If exchange occurs without a change in ion-pair type or external solvation, an HSE estimate of the change in coulombic bonding energy [equation (13)] can be made using the data in Table 2.

$$\mathrm{R}_1^-,\mathrm{Li}^+ + \mathrm{R}_2^-,\mathrm{Cs}^+ \longrightarrow \mathrm{R}_1^-,\mathrm{Cs}^+ + \mathrm{R}_2^-,\mathrm{Li}^+ \quad (12)$$

$$\Delta = [E(\mathrm{R}_1\mathrm{Cs})\varepsilon + E(\mathrm{R}_2\mathrm{Li})\varepsilon] - [E(\mathrm{R}_1\mathrm{Li})\varepsilon + E(\mathrm{R}_2\mathrm{Cs})\varepsilon] \quad (13)$$

Values of this energy for selected pairs of monoanions are given in Table 3. A negative value indicates that the reaction proceeds in the direction shown. In general the favoured situation is that where the smaller cation Li^+ is associated with the more localised (in the HSE sense) anion (*i.e.*, the anion with the greatest coulombic bonding energy) in the product. Also, in general terms, the greater the difference in 'rank order' of the anions R_1^- and R_2^- in Table 2 the greater is the energy change driving the reaction. These predictions are in agreement with a large body of experimental evidence. For example, in the exchange of lithium for sodium or potassium in reaction (14)[69–74] the following considerations apply: it may be the smaller radius of O^- than that of C^-, leading to a greater coulombic bonding energy in ROLi than RONa or ROK, that is the driving force. That driving force should, of course, be enhanced if R′ is a 'delocalised' anion as in the reaction of pentadienyl-lithium[75] with potassium methoxide. In a similar manner preparations of tetra-alkylammonium salts of delocalised anions by reaction (15)[76–78] may well be driven by the greater coulombic bonding energy in $\mathrm{M}^+\mathrm{X}^-$ than is $\mathrm{R}^-\mathrm{M}^+$. In cases where organopotassium compounds are made from organolithium compounds [equation (16)][72,75,79,80] it may well be the greater coulombic bonding energy of CLi than LiBr that provides the driving force. Similarly, in the $\mathrm{Na}^+/\mathrm{K}^+$ exchange reaction (17)[79] the driving force may be the preference of Na^+, the smaller metal ion for the carbanion. Even though the anion is delocalised it probably ranks higher in terms of coulombic bonding energies than does $\mathrm{Ph}_4\mathrm{B}^-$. Whilst it is quite reasonable to argue that all of these reactions are driven by electrostatic forces it should be noted that they all represent preparative procedures and reaction conditions have been chosen so that one product (the product underlined in each equation) in insoluble. It can equally well be argued that it is this insolubility that drives the reaction in the direction shown! A truer test of the predictions inherent in Table 3 would be to study the position of equilibrium in the case of pairs of delocalised ions, where all four partners are soluble and where there are no changes in aggregate or in pair type.

$$\mathrm{RLi} + \mathrm{R'ONa} \text{ or } \mathrm{R'OK} \longrightarrow \underline{\mathrm{RNa}} \text{ or } \underline{\mathrm{RK}} + \mathrm{R'OLi} \quad (14)$$

$$\mathrm{R}^-\mathrm{M}^+ + \mathrm{R'}_4\mathrm{N}^+,\mathrm{X}^- \longrightarrow \underline{\mathrm{R'}_4\mathrm{N}^+,\mathrm{R}^-} + \mathrm{M}^+\mathrm{X}^- \quad (15)$$

$$(\mathrm{X}^- = \mathrm{Cl}^- \text{ or } \mathrm{ClO}_4^-;\ \mathrm{M}^+ = \mathrm{Li}^+ \text{ or } \mathrm{Na}^+)$$

$$\mathrm{RK} + \mathrm{LiBr} \longrightarrow \mathrm{RLi} + \mathrm{KBr} \quad (16)$$

$$(\mathrm{C}_3\mathrm{H}_5)\mathrm{Ph}_2\mathrm{C}^-,\mathrm{K}^+ + \mathrm{Ph}_4\mathrm{B}^-,\mathrm{Na}^+ \longrightarrow (\mathrm{C}_3\mathrm{H}_5)\mathrm{Ph}_2\mathrm{C}^-,\mathrm{Na}^+ + \underline{\mathrm{Ph}_4\mathrm{B}^-,\mathrm{K}^+} \quad (17)$$

The problem of counterion exchange when there are two counterions is rather more interesting. The simplest process is one in which both counterions are exchanged. For example, in reaction (18) the HSE energy for this process is given by equation (19). Values for this energy are given in Table 4. A negative value indicates an increase in bonding energy and hence that there is an HSE driving force for reaction in the direction shown. Note that, as in the monoanion case, these negative values are concentrated on the top right corner of Table 4. Reaction normally proceeds in the direction shown when R_2 is ranked above R_1 in Table 2, *i.e.*, the smaller counterions tend to associate with the more 'localised' anion (the anion with the largest HSE bonding energy).

$$\mathrm{R}_1^{2-},2\mathrm{Li}^+ + \mathrm{R}_2^{2-},2\mathrm{Cs}^+ \longrightarrow \mathrm{R}_1^{2-},2\mathrm{Cs}^+ + \mathrm{R}_2^{2-},2\mathrm{Li}^+ \quad (18)$$

$$[E(\mathrm{R}_1 2\mathrm{Cs})\varepsilon + E(\mathrm{R}_2 2\mathrm{Li})\varepsilon] - [E(\mathrm{R}_1 2\mathrm{Li})\varepsilon + E(\mathrm{R}_2 2\mathrm{Cs})\varepsilon] \quad (19)$$

For these dianion disalts, however, there is an alternative exchange process; one in which just one counterion is exchanged [equation (20)].

$$\mathrm{R}_1^{2-},2\mathrm{Li}^+ + \mathrm{R}_2^{2-},2\mathrm{Cs}^+ \longrightarrow \mathrm{R}_1^{2-},\mathrm{Li}^+,\mathrm{Cs}^+ + \mathrm{R}_2^{2-},\mathrm{Li}^+,\mathrm{Cs}^+ \quad (20)$$

In some cases there is an entropic factor which favours this type of mixed salt formation and this will vary from system to system.* The coulombic factor can, however, be estimated in the normal way from equation (21), and calculated energy values are summarised in Table 5. Once again a negative value indicates that reaction would proceed in the direction shown. It should also be noted that even for the case where $\mathrm{R}_1 = \mathrm{R}_2$ (the diagonal elements of the Table) there is a coulombic driving force for the reaction.

$$\Delta = [E(\mathrm{R}_1\mathrm{LiCs})\varepsilon + E(\mathrm{R}_2\mathrm{LiCs})\varepsilon] - [E(\mathrm{R}_1 2\mathrm{Li})\varepsilon + E(\mathrm{R}_2 2\mathrm{Cs})\varepsilon] \quad (21)$$

By combining the results of Tables 4 and 5, Table 6 can be produced which shows that, purely on HSE grounds, mixing of dianion disalts should sometimes result in transfer of both cations and sometimes just one cation. This is a rather

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* In the case where R_1^{2-}, $2\mathrm{Li}^+$ and R_2^{2-}, $2\mathrm{Cs}^+$ represent single structures but R_1^{2-}, Li^+, Cs^+ and R_2^{2-}, Li^+, Cs^+ each represent a pair of degenerate structures (*e.g.*, the structure with Li^+ on the top surface and Cs^+ on the bottom is indistinguishable from that with Cs^+ on the top and Li^+ on the bottom) this factor at ambient temperature will be *ca.* $R\ln 4$.

unexpected finding. As far as we are aware there is no experimental evidence against which these predictions can be checked.

Conclusions.—Although the application of electrostatics arguments to organic systems always needs to be treated with caution the results described in this paper for group 1 organometallics are quite encouraging. They provide a simple first-order guide to the relative dimensions of group 1 organometallic tetramers and hexamers and to the structures of contact-ion pairs of delocalised organometallics.[30,31] They give results which broadly agree with experimental findings on contact/solvent-separated ion-pair equilibria, triple ion formation, and cation-exchange reactions and provide some interesting predictions, some of which will clearly be susceptible to experimental investigation. It is tempting to suggest a host of further applications, particularly in trying to understand the effect of counterion on processes involving either charge localisation of delocalisation (*e.g.*, rotation about partial double bonds, anionic polymerisation, proton abstraction, *etc.*). It is, however, important to stress the large number of approximations made in these calculations and that while they are useful in understanding general trends the absolute energy values must be treated with caution. We believe the model used provides the best way for search for and display of ion-pair surfaces, but also that it is capable of improvement in several other respects, and we hope that such improvements and further applications will prove possible.

Acknowledgements

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