Preliminary communication

Organic anions

IX *. Applications of point charge and HSE force field models to group 1 organometallic terameric and hexameric aggregates

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(Received August 12th, 1987)

Abstract

The relative dimensions of group 1 $(RM)_4$ tetramers can be accounted for in terms of a simple point charge electrostatic model. Such a model cannot be applied to the equivalent $(RM)_6$ hexamers, but for these a hard sphere electrostatic model is reasonably successful. The findings support the view that the structures of group 1 organometallics are determined principally by electrostatic factors but not the argument that bonding in these compounds is wholly ionic.

Following the pioneering work of Westheimer [2] many force field methods have been developed. Most of these are only appropriate to particular molecular systems; organic molecules of low polarity [3], polypeptides [4], organometallics [1,5] etc. In the case of organometallics such methods are potentially of general utility, and become essential when the systems are too complex for a molecular orbital calculation [6**]. In the case of group 1 organometallics this applies particularly to such species as solvent-separated ion pairs, aggregates, and compounds of the heavier metals. The simplest appropriate force field is normally of the hard sphere electrostatic (HSE) type [1]. HSE force fields, in which point charge electrostatic interactions and hard sphere volume exclusion are the only two types of interaction considered, have long been used to interpret the structure of extended ionic crystalline material [8]. In previous publications we have shown that the HSE model can also account for the structures of some 1/1 [1] and 1/2 [7] group 1 ion pairs.

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* For Part 8 see ref. 1.
** A reference number marked with an asterisk indicates a note in the list of references.

(RM)$_4$ tetramers

Ten years ago Streitwieser showed that an even simpler electrostatic model, in which only point charge electrostatic interactions are considered, could account for the relative dimensions of the methyllithium tetramer [9]. The crystal structure of methyllithium [10] shows a repeating (MeLi)$_4$ unit. Each unit consists of two interpenetrating tetrahedra; one of lithiums and one of methyl ligands as shown schematically in Fig. 1. If we consider that the interaction is purely coulombic (i.e. an equivalent array of positive and negative point charges) then the coulombic energy can be expressed as a function of the C/C bond distance a and the Li/Li bond distance, b. Alternatively, it can be expressed as a function of one bond length, for example a and the ratio $\lambda_1 = b/a$. Since the energy of any array of point charges is given by an equation of the form $A\Sigma(z_i z_j)/r_{ij}$, increasing all the distances r_{ij} by a given factor decreases the total energy by the same factor. Hence a can be regarded as a scaling factor and a "relative coulombic energy", $a \cdot E$, can be defined and expressed purely in terms of λ_1, i.e. the relative sizes of the two tetrahedra. It can further be shown that this relative coulombic energy is at a minimum when $\lambda_1 = b/a = 0.783$ [9]. In methyllithium the ratio b/a is found experimentally to be 0.73; remarkably good agreement for such a simple model! Streitwieser has further argued [9] that if we consider the negative charge on CH_3^- to be centred not at the carbon but 0.26 Å from the carbon (i.e. in an sp^n hybrid orbital) the fit between prediction and experiment can be made more exact. However, Schleyer long opposed Streitwieser's claim of the highly ionic nature of organolithium compounds. He has argued that the agreement between the point charge electrostatic model and experiment in the case of (MeLi)$_4$ is fortuitous, and has compared the predicted ratio of 0.783 with those derived for a series of "largely ionic" (LiX)$_4$ compounds by "good quality ab initio MO calculations" [11]. These results are displayed in Fig. 2, and it will be seen these MO calculations generally predict a larger value for λ_1, the average of the values given in Fig. 2 being 0.84 ± 0.13. It is, however, more significant to compare the values from the electrostatic model with experimental results, and so in Fig. 2 we have also collected together X-ray data for other relevant group 1 (MR)$_4$ and (MX)$_4$ tetramers. Some of these are simple organometallics, but in some the ligand is coordinated through oxygen or nitrogen rather than carbon, and in others there is additional coordination of a neutral ether or tertiary amine ligand to the lithium. Some of the data used
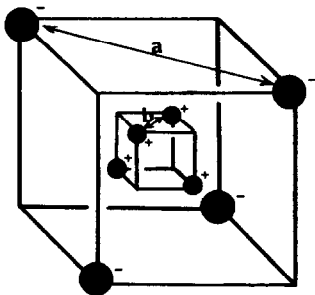

Fig. 1. Schematic representation of the structure of the methyllithium and related (RM)$_4$ and (MX)$_4$ tetramers.
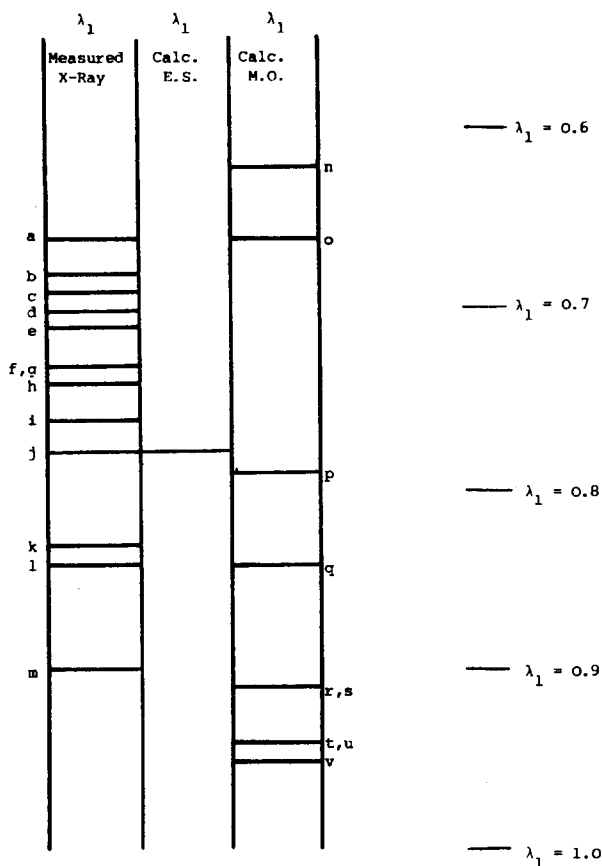
Fig. 2. Values of the ratios of bond lengths ($\lambda_1 = b/a$ see text) obtained by X-ray crystal structure determinations, predicted by a point charge electrostatic model and calculated by good quality MO methods. In cases where the tetrahedra are not symmetrical and full data is available bond lengths (Å) have been averaged: (a) $[Li^+, CH_3^--CHCH_2CH_2OCH_3]_4$; average C–C 3.78; average Li–Li 2.48 [12]; (b) $[Li^+, Et^-]_4$; average C–C 3.74; average Li–Li 2.55 [13]; (c) $[Li^+, C_6H_4\text{-}2\text{-}CH_2NMe_2^-]_4$, average C–C 3.71; average Li–Li 2.58 [14]; (d) $[Li^+, Me^-, Me_2NCH_2CH_2NMe_2]_4$, average C–C 3.64; average Li–Li = 2.56 [15]; (e) $[Li^+, C_5H_7O^-, THF]_4$, average O–O 3.27; average Li–Li 2.31 [16]; (f) $[Li^+, Me^-]_4$ [10]; (g) $[Li^+, C_6H_5^-, Et_2O]_4$; C–C 3.69; Li–Li 2.70 [17]; (h) $[Li^+, C_6H_5^-, Et_2O]_3 [Li^+, Br^-]$; average C–C and C–Br 3.67; average Li–Li 2.90 [17]; (i) $[Na^+, CH_3^-]_4$, average C–C 4.15; average Na–Na 3.16 [18]; (j) $[Li^+, C_3H_5]_2[Li^+, Br^-]_2$, average C–C, C–Br, Br–Br 3.73; average Li–Li 2.90 [19]; (k) $[Li^+, {}^-N=CPh_2, NC_5H_5]_4$, average N–N 3.19; average Li–Li 2.66 [20]; (l) $[Li^+, Cl^-, OP(NMe_2)_3]_4$, average Cl–Cl 3.67; average Li–Li 3.10 [20]; (m) $[Li^+, {}^-CH_2COBu^t]_4$, average O–O 2.93; average Li–Li 2.64 [16]; (n) $[Li^+, Me^-]_4$ [21]; (o) $[Li^+, NH_2^-]_4$ [11]; (p) $[Li^+, NH_2^-]_4$ [11]; (q) $[Li^+, OH^-]_4$ [11]; (r) $[Li^+, H^-]_4$ [11]; (s) $[Li^+, F^-]_4$ [11]; (t) $[Li^+, F^-]_4$ [22]; (u) $[Li^+, H^-]_4$ [23]; (v) $[Na^+, H^-]_4$ [22].

were directly available from the literature or the CSSR data base, but in some cases (for example [12,15,18]) insufficient M^+ and X^- positions were given in the unit cell and it was necessary to generate the remaining positions using the appropriate symmetry operations *.

The agreement between the experimental data and the simple point charge model remains encouragingly good. The average value of the ratio λ_1 for the X-ray results given in Fig. 2 is 0.75 ± 0.07. It is important to note that in the point charge model the net electrostatic interaction is attractive, and in the absence of closed shell repulsive interactions the system would collapse towards a point! In this sense there is no need to invoke multi-centre covalent bonding [24] in order to explain the stability of the aggregate. It would however be misleading to use this agreement between theoretical and experimental values to support the claim that bonding in these systems is almost wholly ionic [25] with no multicentre covalent component. All that is required is that the bonding is predominantly ionic. The point charge model predicts the same ratio λ_1 for any array of this type provided only the charges on X^- and M^+ are equal. They could well be less than ± 1.0. Experimental evidence seems to require at least a little covalent character in these compounds; for example, to explain the presence of ^{13}C–^{7}Li spin–spin coupling in $(MeLi)_4$ [26].

(RM)₆ Hexamers

In bonding in $(MX)_4$ is predominantly ionic and electrostatic interactions determine the dimensions of the system, then this should be true not only for $(MX)_4$ but also $(MX)_6$ aggregates, and since X-ray crystallographic structures for two of these are now available (cyclohexyllithium [27] and 2,2,3,3-tetramethylcyclopropylmethyllithium [28]) we have tested this suggestion. Such an approach does work, but it is necessary to use an HSE rather than a point charge model. In the known $(LiR)_6$ aggregates the lithiums are arranged as a trigonal antiprism surrounded by a trigonal antiprism of R^- groups as shown schematically in Fig. 3. If the R^- and M^+ components of such an array are replaced by point charges, the dimensions of the system and hence the electrostatic energy E can be expressed in terms of the four unique interpoint distances c, d, e, and f, or the energy relative to one of these
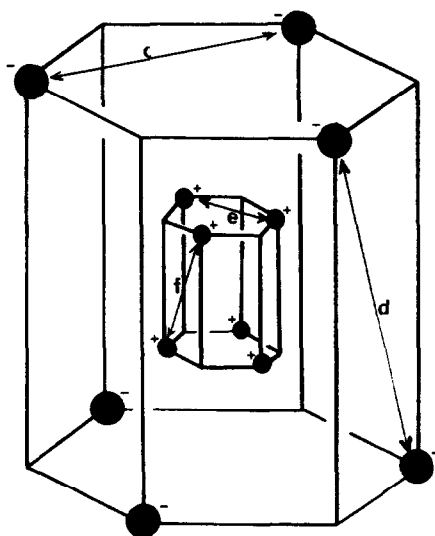

Fig. 3. Schematic representation of the structure of alkyllithium $(RLi)_6$ hexamers.
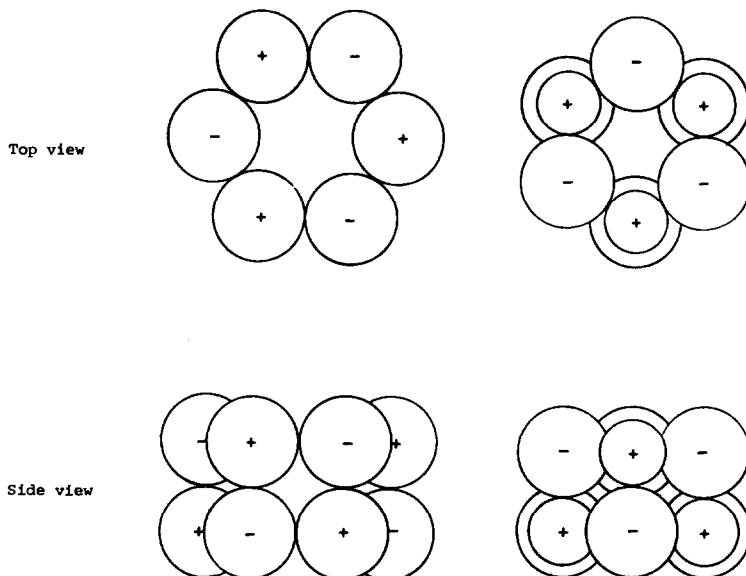
Fig. 4. Energy minima for $(RM)_6$ in the HSE model; (4a) $r_+/r_- = 1$; (4b) $1 > r_+/r_- > 0.414$.

distances, say c, in terms of three ratios, most conveniently $\lambda_2 = c/d$, $\lambda_3 = e/f$, and $\lambda_4 = e/c$, which define the shape of the R^- trigonal antiprism, the shape of the Li^+ trigonal antiprism, and the relative sizes of the two trigonal antiprisms, respectively. λ_4 can adopt any positive value but λ_2 and λ_3 must lie between 0 and 1.73 *. Values of λ_2, $\lambda_3 < 1$ represent a long thin trigonal antiprism. λ_2, $\lambda_3 = 1$ represents a regular octahedron and as λ_2, λ_3 tends towards 1.73 the trigonal antiprism becomes short and fat and finally collapses to give a circle of six equally spaced points. Computer programs have been written ** to calculate and minimise the coulombic energy E as a function of the bond lengths c, d, e, and f and/or the relative coulombic energy, c. E, as a function of the ratios λ_2, λ_3 and λ_4. It was found that for an array of point charges the minimum was formed at $\lambda_2 = \lambda_3 = 1.73$ and $\lambda_4 = 1.0$; i.e. the two trigonal antiprisms collapse to circles of point charges that then collapse into each other! If, however, the point charges are replaced by hard spheres different results are obtained. The result for the simplest case where the spheres representing the anion and cation are assumed to have equal radii ($r_+/r_- = 1$) is shown in Fig. 4a. The most stable arrangement is found to be a symmetrical ring of alternating positively and negatively charged ions placed directly above a similar ring, and corresponds to two interpenetrating trigonal antiprisms in which the ratios λ_2, λ_3, and λ_4 are 1.23 **, 1.23 **, and 1.0, respectively. This shows a reasonable agreement, at least in the first two values, with the values found experimentally for tetramethylcyclopropylmethyllithium (λ_2, λ_3, $\lambda_4 = 1.14$, 1.21,

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* $2 \cos 30°$.

**   Based on the NAGF Mark II library routine E04UAF which finds a minimum of a function of several variables subject to fixed bounds on the variables and non-linear constraints, and which solves the minimisation by a quasi-Newton method.
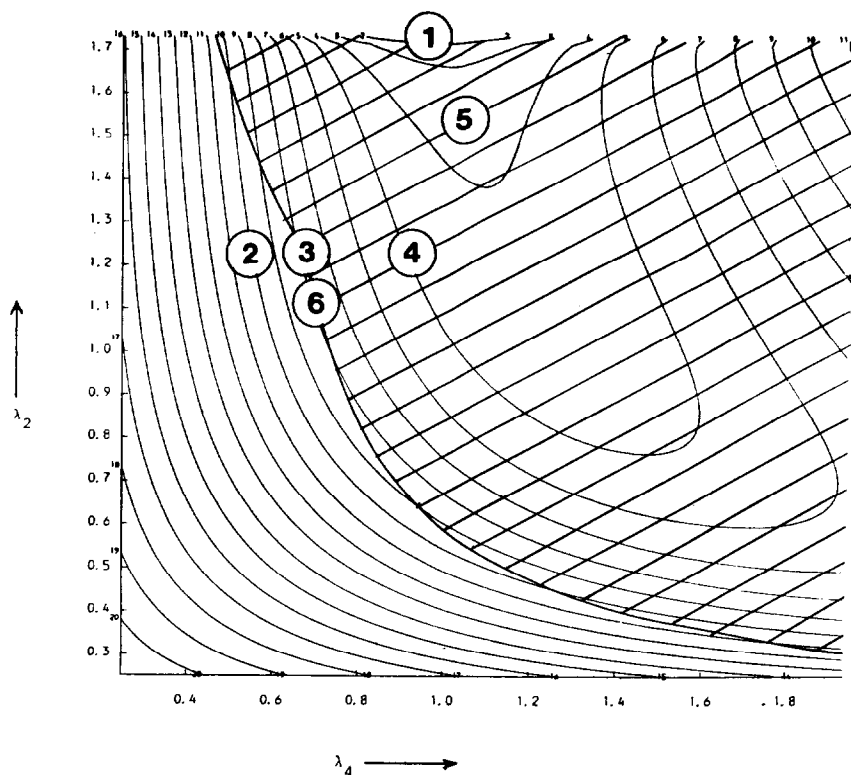
*** $(1/\sqrt{2}) \cos 30$.

Fig. 5. Electrostatic energy contours for the $(MR)_4$ system assuming e 2.97 and f 2.46 Å. See text.

0.74) and cyclohexyllithium (λ_2, λ_3, $\lambda_4 = 1.13$, 1.25, 0.73). If the two ionic radii are made unequal the solution remains the same (λ_2, λ_3, $\lambda_4 = 1.23$, 1.23, 1.0) down to the limit $r_+/r_- = 0.414$ * [8]. Beyond this limit solutions are found to be $r_+/r_- = 1/3$ (λ_2, λ_3, $\lambda_4 = 1.15$, 1.30, 0.99), $r_+/r_- = 1/4$ (1.07, 1.29, 0.99), 1/5 (1.03, 1.18, 0.99), 1/6 (1.01, 1.12, 0.99), 1/7 (1.00, 1.05, 0.97), 1/8 (1.00, 1.02, 0.94), 1/10 (1.00, 0.95, 0.90).

A related approach to the same problem is to regard the inner trigonal antiprism of lithium ions as fixed in space and to then determine the optimum position for the counterions. That is distances e and f are taken as fixed and the optimum value of c and d (or λ_2 and λ_4) determined. This approach has the advantage that the results can be displayed graphically as shown in Fig. 5, where we have assumed e 2.97 Å and f 2.46 Å (as in tetramethylcyclopropylmethyllithium [28]). $\lambda_2 = c/d$ is plotted on the vertical axis and $\lambda_4 = e/c$ on the horizontal axis, and points of equal electrostatic energy are connected by equally spaced contour lines. As may be seen, the lowest energy point on this surface is at point 1, $\lambda_2 = 1.73$; i.e. there is a ring of point charges. This, however, would bring the R^- and Li^+ within the normally accepted contact distance. If we accept a more realistic hard sphere model we find that a large section of space in Fig. 5 is unavailable to the alkyl ligands. In Fig. 5 we

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* $\sqrt{2} - 1$.

have shaded this exclusion region for a minimum C–Li distance of 2.27 Å. Within the shaded area C–Li is < 2.27 Å, outside the area C–Li is > 2.27 Å, and positions along the dividing line represent different trigonal antiprism arrangements where the ions are in contact. Positions on this line are seen to always be more favourable than those in the unshaded area (where the ions are separated), and the minimum energy position along this line is at point 3. Points 2, 3, 4, 5 show the equivalent positions predicted for hard sphere models with minimum C–Li distances of 2.77, 2.27, 1.77, and 1.27 Å respectively. Note that position 3 is close to the experimental values of λ_2 and λ_4 for cyclohexyl and 2,2,3,3-tetramethylcyclopropylmethyl-lithium (point 6 and that points 2–4 are all close to the $\lambda_2 = 1.23$ position, and in positions where R⁻ bridges equally to three counterions.

Conclusion

A point charge or HSE model is able to provide a first order account for the relative dimensions of group 1 $(MX)_4$ tetramers and $(MX)_6$ hexamers providing further support for the argument that bonding in these systems is determined principally by electrostatic factors.

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