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A molecular orbital study of the bonding in complexes of lithium with polynuclear aromatic hydrocarbons

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In a preliminary investigation of the bonding between the sub-lattices of lithium and of graphite in intercalation compounds, molecular orbital calculations are performed on systems of Li atoms π complexed to one or both sides of polynuclear aromatic hydrocarbons. Energy wells calculated reveal possible sites offered to the Li atoms above the aromatic plane to form complexes in both central and edge regions of the molecule. The influence of additional complexed Li atoms on the migratory tendency of a given Li atom is also investigated, and observations made on the effect of the complexed Li atoms on the C–C bonds of the hydrocarbon.

Key words: Polynuclear aromatic hydrocarbons — Lithium π complexes — Graphite-lithium intercalates — Barriers to migration — Charge transfer

1. Introduction

This work forms part of a theoretical treatment of the association between alkali metal atoms and planes of carbon atoms such as those contained in the lattices of such extensively electron-delocalized systems as exist in graphite and semiconducting polymers. We direct our attention to lithium atoms, the structures of whose π complexes with the rings of some benzenoid polycyclic molecules have been determined from X-ray studies [1]. We intend, in a subsequent study, to use the findings of this investigation in a theoretical treatment of the migration of lithium atoms or ions between the extended planes of an intercalated lattice.

While the long range (Madelung) contribution to the energy of a lithium intercalate may be satisfactorily calculated by lattice simulation methods [2] the short range interactions require a more detailed knowledge of the nature of the association between the lithium and carbon sublattices. If this interaction were a purely ionic one between atomic species bearing integral charges standard methods [3] could be used to derive a suitable short-range potential. However although the amount of charge transferred from the Li atom to the carbon sublattice, as deduced from various methods - electronic heat capacity [4], ^{7}Li Knight shift [5], ^{7}Li quadrupolar couplings [6] and positron annihilation [9] - is not sufficiently consistent to quote a reliable figure, it seems very probable that the electron transfer is incomplete [7, 8], and that a substantial degree of covalency must be present in alkai-graphite intercalation compounds. Moreover the electron delocalization associated with the carbon sublattice suggests the possibility of activation of a given lithium site by the presence of a second Li atom complexed at a neighbouring site. It is important to elucidate the nature of such aspects of the short range interactions so that we may evaluate the feasibility of lattice simulation calculations on alkali metal intercalate systems.

2. Polycyclic aromatic hydrocarbons

Secondary electron spectroscopy [9] and band structure calculations [10] show that while the valence electronic energy bands of a single graphite lamella are affected by intercalation if they are in the region of the Fermi level, the inclusion of additional carbon lamellae (which would obtain in higher stage intercalates) has an insignificant effect on the band structure, showing that a discussion of the bonding of the alkali metal sublattice to the graphite sublattice can be largely confined to a single Li layer and just the carbon lamellae adjacent to this layer [11]. This result is consistent with the findings of the same calculation that the electronic charge transferred from the Li sublattice is found almost completely on the adjacent carbon layers and only insignificantly on subsequent ones. In an attempt to understand the nature of the binding we select the analogous systems of π complexes of Li with the benzenoid rings of polycyclic aromatic hydrocarbons as model compounds on which to perform molecular orbital (MO) calculations, and for which experimental measurements are available which may be "carried over" to the intercalate compounds for which they model. It is not difficult to find similarities between aromatic molecules and graphite. Bond lengths in both systems demonstrate extensive π electron delocalization [12]. The intercalation properties of graphite are reflected, in aromatic systems, (I) in the liquid state by metallocene formation [13], and (II) in the solid state by the occlusion of guest atoms and molecules to form stacking sequences [14]. Reminiscent of the latter is the well-known ability of polynucleotides [15] to occlude guest species between their "stacked" purine/pyrimidine bases. Ionization energies of solid aromatic hydrocarbons decrease with increasing molecular size [16], along series such as naphthalene (6.75 eV), anthracene (5.65), tetracene (5.35) and pentacene (5.1), towards the graphite value of 4.7 eV.

The foregoing remarks concerning the role of the carbon lamellae adjacent to the Li layer imply that the proposed calculations will not require stacks of hydrcarbon molecules to represent the grphite lattice—the intercalate could, for purposes of investigating gross features of the bonding, be represented by a (hydrocarbon)-(Li...)-(hydrocarbon) three-layer sandwich, in which the Li atoms occupy sites on a plane parallel to those of the aromatic hydrocarbon molecules.

Since current lattice simulation calculations [2] require short range interactions to be described by two-body functions we shall perform our calculations on "open sandwich" complexes, (hydrocarbon)-Li, in which the Li atom is at a site on a plane parallel to the aromatic plane. The possible effect of a *second* Li atom on this interaction will be investigated by placing this atom on another site, on either side of the aromatic plane.

2.1. Selection of the hydrocarbons

The hydrocarbon complexes must be sufficeintly large to exhibit features of a graphite intercalate, but small enough to enable the necessarily large number of calculations on the system to be performed economically and in a resonable time.

Since the π MOs, and hence electron delocalization, play a critical role in the bonding, we should select a molecule consisting of several rings. Such a molecular system would involve an excessive computing time if treated by non-empirical (*ab initio*) methods on available computers; we have therefore decided to use a semi-empirical method, which is known to provide reliable ground-state molecular geometries on energy minimisation [17], but for which there may be a systematic over-estimation of the depths of the energy wells.

A polycyclic benzenoid hydrocarbon of 22–25 C atoms with one or two complexed Li atoms requies a CPU time of about one hour on a DEC 2060 computer using a CNDO/2 program [18]. Thus as well as benzene and naphthalene we selected the molecules pentacene(I), chrysene(II), coronene(III) and benz-1,2-perylene(IV) illustrated in Fig. 1 to test the constancy of the binding of the Li atom(s) to different topological features such as might be found at the edges of graphitic lamellae, where the intercalation mechanism must start.

2.2. Benzenoid character of the rings

An interesting feature of benzenoid polycyclic hydrocarbon molecules lies in the differing degree of benzene-like character of the various rings, which has been well discussed by Clar [19]. According to Clar, in such a molecule only certain rings are fully benzene-like, and they are those which appear in a *unique* classical valence bond structure in which the *maximum* number of cyclohexatriene rings (constituting aromatic sextets and hence conferring fully benzene-like character on those rings) are connected by a set of non-conjugated single and/or double bonds. Of the four molecules in Fig. 1 only II and IV contain a set of ring-localized aromatic sextets shown in Fig. 1a as inscribed circles in rings A, C and E: in I and III the aromatic sextets cannot be fully associated with particular rings but must be shared, as indicated by the Clar migration arrows. This picture is reflected

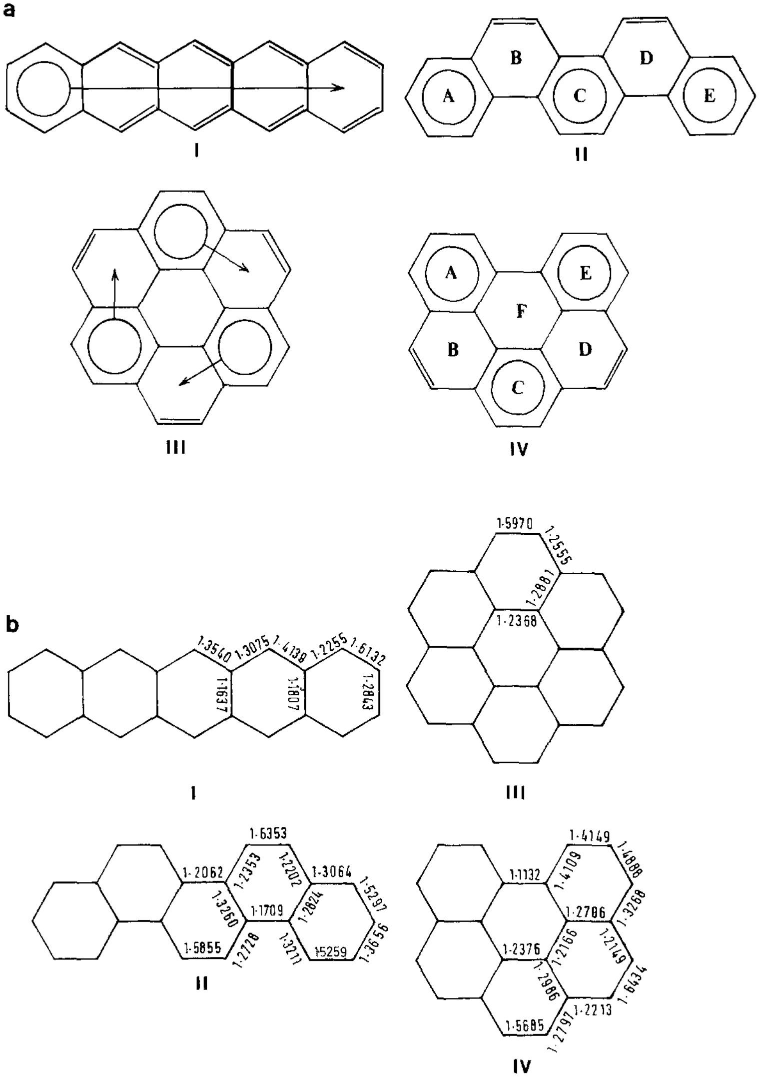


Fig. 1. (a) Pentacene (I) chrysene (II), coronene (III) and benz-1,2 perylene (IV) written in the Clar convention (see [14] and text). (b) Wiberg bond orders of the four aromatic hydrocarbons I to IV

in the Wiberg bond orders indicated in Fig. 1b. These values show the rather smaller degree of bond alternation in those rings which the Clar description presents as benzene-like than in those in which there is either *no* aromatic sextet, or in which it is shared. Clar's theory of aromatic hydrocarbons would clearly be of relevance to this work if the stability of a Li complexed at a site depended on the degree of benzene character of the particular ring. If this should be the case the possibility should also be investigated, that such a complexed Li localizes the aromatic sextet to that ring, thus fixing other sextets to predictable rings in the aromatic network, and hence creating preferred sites for the intercalated atoms.

Finally it must be emphasized that this paper is not a theoretical investigation on experimentally well-defined chemical species - no argument is made for the existence of the cationic lithium aromatic hydrocarbon complexes which feature in this work. Rather our purpose is to postulate chemically feasible structures to which computational methods may be validly applied in order to examine the nature of the bonding in the technologically important related species - the intercalation compounds of Li with graphite and with semiconducting carbon chains.

3. The structures of Li intercalates

First stage Li intercalate has the empirical formula [20] LiC_6 and the x-ray diffraction is best interpreted [21, 22] by postulating successive C atom lamellae which are related by a pure translation along the C axis of the hexagonal lattice system, thus generating the lamellar sequence AAA... with A–A separations of 3.706 Å. This simple translational periodicity contrasts with the sequence in pristine graphite [23] in which successive lamellae are displaced to produce the alternating sequence ABAB... with an A–B spacing of 3.35 Å.

The empirical formula, together with the tendency of metal atoms (including Li) to form π bonded complexes with small rings of aromatic hydrocarbons, in which the metal atom lies approximately on the ring axis [1], suggests that the Li atoms in "Li graphitide" (1st stage Li intercalate; LiC_6) are located in planes between the C lamellae in such a way that each Li resides over the centre of a C ring, each C atom being associated with 1/6 of a Li atom. The sequence of the Li planes along the C axis is less certain than that of the C planes; there is disagreement in the interpretation of the X-ray data, various groups claiming that the simple translational sequence $\alpha\alpha\alpha$... [21] or the displaced sequence $\alpha\beta\gamma\alpha$... [22] fit the data best. In the former sequence a C_6 ring with a Li atom complexed on one side of it will have another Li complexed on the other side, thus giving rise to "straight line" chains...-(ring)-Li-(ring)-Li-(ring)-... along the C axis, written $A\alpha A\alpha$... or just $A\alpha$. In the $\alpha\beta\gamma\alpha$ sequence, where there are three possible sites for the Li atom in successive layers, the "columns" of Li atoms of the $A\alpha$ structure are replaced by helices of Li atoms. Despite the inconclusiveness of the x-ray data in distinguishing between these structures, a number of theoretical investigations have assumed $A\alpha$ [10]. It may be instructive to examine the facility of our polycyclic aromatic hydrocarbons to undergo π complexation to more than one lithium atom, on the axes of various rings, on either the same side, or on different sides, of the aromatic plane.

4. Structures of the model compounds

Assuming C_6 rings which are undistorted by either their position in the hydrocarbon molecule or by complexation to the Li atoms, we use a uniform C–C bond length of 1.40 Å, and the Li atoms are placed at a height of 1.8 Å from the aromatic plane. The latter value was chosen, not only because it is equal to half the measured C-lamellar spacing in 1st stage Li graphite intercalate [20, 21], but because it corresponds to the averaged x-ray distances of Li from the centres of rings in a number of lithium-aromatic-ring complexes [1]. Moreover, the energy-minimised height of Li above various rings in the model hydrocarbons I to IV varies from 1.8 to 1.9 Å and shows only a small change (~+0.05 Å) if another Li atom is already complexed at a neighbouring site in the same molecule.

Although a sufficiently large volume of the LiC_6 lattice possesses a net charge of zero, we shall avoid the complications arising from open-shell configurations (which would result from the hydrocarbon-lithium radical complex RH...Li) by removing the excess electron and considering the charged species $[RH...Li]^+$ and, for consistency, $[Li...RH...Li]^{2+}$ so that our investigation is essentially on aromatic hydrocarbons with Li^+ ions. However, provided that the aromatic hydrocarbon molecule is large enough to model a graphite lattice for the purposes of investigating the complexing characteristics of a single ring, it is assumed that the presence of small charges on the Li complexes, when spread over an approximately 20-carbon-atom molecule would not seriously affect the description of the ring-Li association.

5. Results

A Li atom (ion) was introduced in various positions at a constant height of 1.8 Å over the plane of each of the aromatic molecules considered and the total molecular electronic energy calculated by the CNDO method. By this means the regions of high and low energy encountered in a migratory trajectory of the Li atom are revealed as a succession of peaks and troughs.

Next, keeping a second Li atom fixed at a distinct site, the influence of this atom on the former migration is examined.

All the calculations, with the exception of those on one of the $[\text{pentacene } Li_2]^{2+}$ complexes (see section 5.2) yielded net charges on the Li atoms in the range +0.20 to 0.35e, irrespective of whether one or two lithium atoms were coordinated. The remaining charges were rather evenly distributed over the hydrocarbon in such a way that all net atomic charges were small ($0 < q < 0.05$e). The minimum energy positions of the Li atoms along the sixfold axes of various rings were also investigated but were found to lie in such a small range (height h above the molecular plane was 1.8 to 1.9 Å irrespective of the position of the ring in the molecule, or of the presence or absence of a second Li atom) that no further investigation of h was deemed necessary. Also, although not reported in the subsequent sections of this paper the variation of energy with h yielded a parabola permitting the extraction of a Li-ring force constant k of 19-21 eV Å^{-2}. Due to the basis set superposition error [24] inherent in CNDO these values of k are probably too large. While there are no experimental data on the complexes considered in this work, Fritz [25] quotes a force constant of ~1 mdyne Å^{-1} (6.2 eV Å^{-2}) for Li complexed along the 5-fold axis of a cyclopentadienyl ring.

5.1. Small hydrocarbon molecules: benzene and naphthalene

In order to test the effect of the size and nature of the aromatic hydrocarbon on the migration properties of π complexed Li, the energies of [benzene.Li]$^+$ and of [naphthalene.Li]$^+$ were followed as a function of the position of the Li atom across the molecule, and the results are shown in Fig. 2.

Although the zero of the energy scale in the diagram has formally beeen taken as the calculated energy of the complex when the Li atom is at an infinite distance from the hydrocarbon the basis set superposition error precludes the placing of too large a reliability on these energies in an absolute sense. However the success of the CNDO/2 method in geometry-optimization allows us some measure of confidence in the order of the stabilities of the configurations generated when the Li atom migrates between sites without changing its distance from the aromatic plane, and thus in the relative magnitudes of the barriers.

Figure 2 shows an energy rise of ~3.0 eV when Li moves from its minimum energy site over the centre of a ring to a position over an exterior C–C bond of the molecule, while on crossing the inter-ring bond in naphthalene it encounters a lower barrier of 1.75 eV.

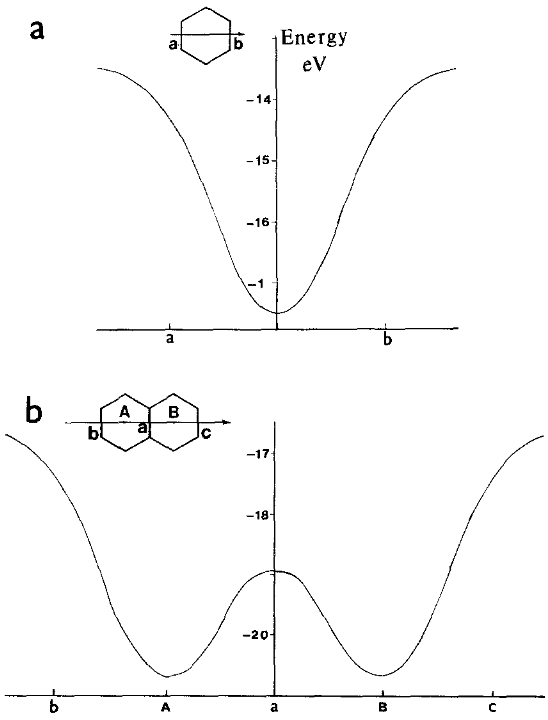


Fig. 2. Potential energy variation during the linear migration of Li$^+$ 1.8 Å above the aromatic planes of (a) benzene and (b) naphthalene

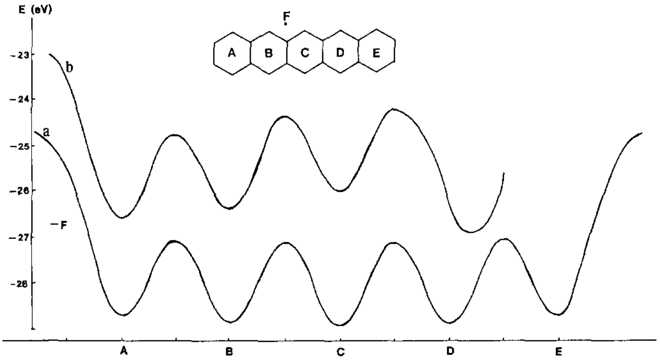


Fig. 3. (a) Migration of Li above the long axis of pentacene (I). (b) As (*a*) but with a second Li atom fixed at the centre of ring *E*

5.2. Pentacene

This molecule should show features of a set of one-dimensionally annellated benzenoid rings, constituting an acene series.

The lower curve in Fig. 3 shows the variation in the potential energy monitored by a Li atom moving over the molecular surface, parallel to the long axis of the molecule. We find a sequence of peaks and troughs which reveal very little preference for any site: that over the centre ring C is only 0.05 eV more stable than those on the neighbouring rings *B* and *D*. The barriers between successive rings are fairly uniform, with a range of 1.66 to 1.84 eV.

The point *F* on the energy axis at −26.74 eV denotes an energy minimum at a level just above the inter-ring barriers, for a site *outside* the molecule. Each of these sites is situated 1.1 Å from a C atom shared by two rings, and 1.8 Å above the moleuclar plane.

The upper curve shows the corresponding migration energy of a Li atom over a pentacene molecule when a second Li is kept fixed over the centre of ring *E*. Although most of the inter-ring barriers are in the former range, there is now a deep trough over ring *D* which lies 0.93 eV below that associated with its neighbouring ring *C*, and a consequently large barrier between rings *C* and *D*, 2.72 eV. These features taken together impose an impediment to the Li atom to migrate from ring *D* where it enjoys an unexpected close association with the lithium in ring *E*. Unlike the positive charges found on the Li atoms in all the other complexes in this investigation, negative charges are borne by the Li atoms on sites *D* and *E* (−0.64 and −0.53e respectively). We shall discuss the significance of this partiular $[\text{pentacene.Li}_2]^{2+}$ complex in Sect. 6.

5.3. Chrysene

The potential energy curve for the migration route of Li atom over the centres of the rings is the continuous line in Fig. 4. As was the case for single-Li migration

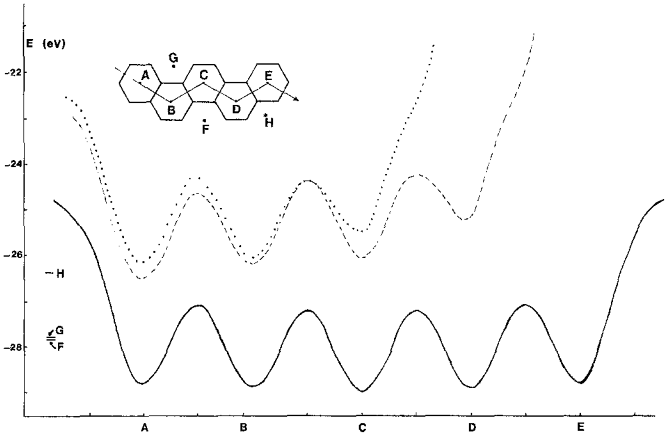


Fig. 4. Migration of Li over chrysene (II). ———: single Li atom. ----: migration with a second Li atom fixed above ring *E*. ······: migration wth second Li atom fixed above ring *D*

over the pentacene rings, there is no highly-favoured site in any of the rings (the least favoured sites, A and E, are only 0.2 eV above the most favoured one, *C*) - hence a Li atom could associate with any of the rings. The barriers to migration between adjoining sites are again in the narrow range 1.67–1.87 eV.

The points on the energy axis at −27.81, −27.77 and −26.38 eV denoted *F*, *G* and *H* respectively refer to sites found outside the molecular framework. The sites at *F* and *G* are very close to those that would obtain if the half-rings constituting the 'bay regions' in these parts of the molecule had been full benzenoid rings, while that at *H* is analogous to the *F* site in pentacene (though its energy is rather greater with respect to the ring sites than the latter).

When Li is complexed at ring *E* (the broken curve in Fig. 4) the site over the adjoining ring *D* becomes considerably destabilized with respect to the most favoured one, which is now ring *A*, the furthest from *E*. Sites *B*, *C* and *D* lie respectively 0.30, 0.44 and 1.33 eV above site *A*. Since these quantities are large in comparison with kT we conclude that the establishment of a Li atom on a ring site substantially destabilizes sites in its vicinity.

Similarly, keeping the fixed Li atom over ring *D*, the dotted curve shows that the adjoining ring *C* becomes destabilized by 0.44 eV with respect to ring *A*, which is still the lowest energy site.

5.4. Coronene

We might expect the greater arial extent of this hydrocarbon to represent some aspects of graphite intercalation more closely than the molecules of the previous sections.

Results shown in Fig. 5 for the three Li atom migration routes denoted 1, 2 and 3 imply that there is no strongly favoured or disfavoured ring site in coronene,

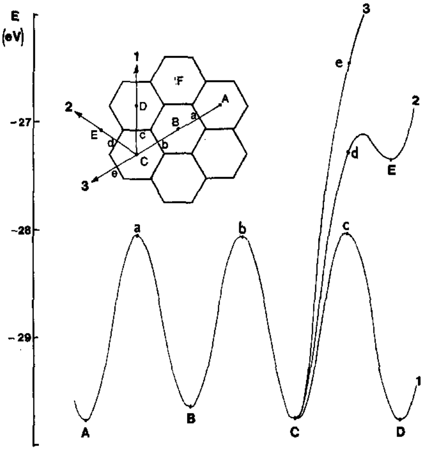


Fig. 5. Three migratory routes for a Li atom over the plane of coronene (III)

an outer ring such as *A* offering a site which is only 0.127 eV lower than that above the central ring *B*. Since the total molecular energies when Li is over either of the two types of inter-ring bond *b* or *c* are almost equal, the barriers presented to inter-ring migration lie in a small range (1.58–1.74 eV).

The curve for route 2, in which the Li atom exits the molecule via bond *d*, reveals a high-energy minimum at point *E* which is analogous to those we noted in pentacene and chrysene. The position *E* is over the extension of bond *c*, 1.1 Å from the outer atom. In order to pass through it our route 2 has deviated slightly to the right after bisecting the bond *d*, and encountering a small (0.24 eV) barrier.

The effect of a second Li atom is shown in Fig. 6a, where one Li atom is fixed over ring *A* while the second monitors the potential energy at other sites in the molecule, over ring centres and bond centres (as usual at 1.8 Å over the molecular plane). The energies in eV, relative to the most stable site (above the centre of ring *C*) are written on the rings or on the bonds, as appropriate. Clearly a Li atom over ring *A* destabilizes sites in neighbouring rings by ~0.5 eV leaving the relative energies (including the barrier range) in the rest of the molecule unaffected.

Figure 6b shows the total energies of [coronene . Li_2]$^{2+}$ complexes, referred to the same zero as in Fig. 6a, but in which the two Li atoms are now complexed to opposite sides of the aromatic plane. The + and − signs refer to the two sides

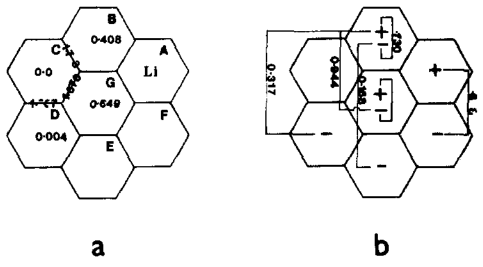


Fig. 6. (a) Potential energy of a Li atom at various sites (over the centres of rings and of bonds in coronene (III) when a second Li atom is over ring *a*. The energies are in eV measured relative to the most stable configuration (Li atoms over *A* and *C*). (b) As for (a) but the two Li atoms are on opposite sides of the molecular plane, as denoted by the + and − signs

of this plane so that, for example, the energy of the complex, in which one Li is complexed "above" an external ring while the other is "below" the central ring, is 0.944 eV higher than that of the minimum-energy structure. From a comparison of the figures (*a*) and (*b*) of Fig. 6 we conclude that *trans*-lamellar sites are less stable than cis-lamellar ones. An interesting implication of this is that the "deactivation" of one site by a Li atom in a neighbouring one is not due simply to repulsion between the two atoms. For example, Li atoms above rings *A* and *F* give rise to a relative energy of 0.408 eV; but if we move the Li "above" *F* to the corresponding site "below" the ring the energy is 0.888 eV, despite the (nearly twofold) greater separation of the Li atoms. Since the same carbon orbitals are offered to the second Li atom, whichever side of the aromatic plane it approaches, it would appear that the extra stabilization of *cis* structure may be ascribed to two factors which enforce one another. Since we find that the Li species in these complexes are not bare ions we might expect a degree of covalency between them at short distances. In adjacent-ring sites this distance is 2.42 Å, which is close to the bond length of 2.67 Å found in the Li_2 molecule [26]. Another reason for the lower energies of the *cis* structures is that the polarization of the electron density of the hydrocarbon by one lithium atom is communicated to other regions of the molecule, thus facilitating the association of a second lithium atom on the *same* side of the molecule.

The higher energies for the structures in which the Li atoms lie on either side of the same ring (~1.7 eV) compared with those in which the atoms lie on different sides of adjacent rings (~0.9 eV) would suggest (see Sect. 3) $A\alpha A\beta A\gamma$ to be a more favoured sequence. This conclusion is similar to that made by Metzger [27] when he calculated the cohesive energies of C_6Li for the two possible structures $A\alpha A\beta A\gamma$ and $A\alpha$.

5.5. Benzperylene

This molecule is included in our selection because of the presence of a "bay-region" ring fragment *G*. Apart from the important physiological properties of aromatic hydrocarbons containing such edges (they are carcinogenic [28]) we have seen in our results on chrysene (Sect. 5.3) that π complexation at a site associated with a ring fragment such as *G* is possible, but has a smaller degree of stabilization. Also, *G* contains the configuration of *cis*-polyacetylene which is known to be able to occlude alkali metal atoms, including lithium [29]. It is therefore important to examine the complexing ability of such shapes.

The continuous curve of Fig. 7(ii) described a Li atom migrating from the outermost bond *a* of *C* through *F* into the bay region *G*. Again there is the almost insignificant difference (0.14 eV) between the binding abilities of the sites associated with rings *C* and *F*, and barriers of 1.6 and 1.7 eV. Unlike the potential wall encountered at bond *a*, the bond *c* between *F* and *G* presents a 1.73 eV barrier (to an outwardly migrating Li) of the same magnitude as those encountered at internal bonds in the molecule. Having surmounted this barrier the Li atom finds a site which is over the centre of the region *G* as if it were a true ring. The

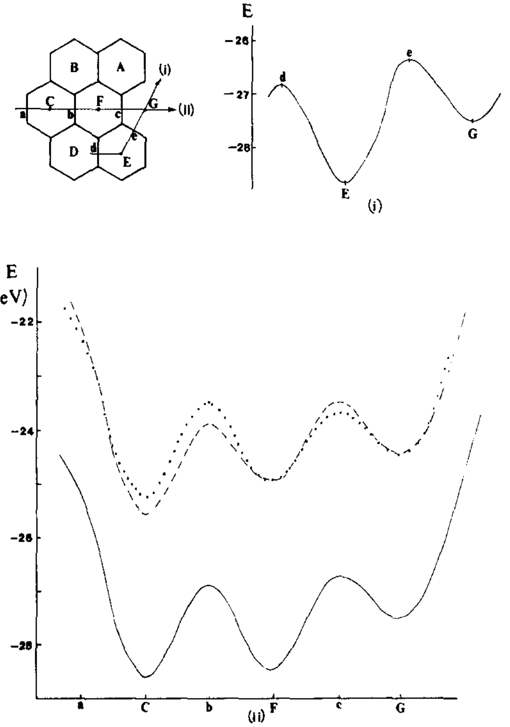


Fig. 7. (i) and (ii) *Continuous lines*: two routes for the migration of Li over the surface of benzperylene (IV). ----: second Li fixed at *A*. · · · · · ·: second Li fixed at *B*

depth of the well (0.75 eV) below the *F*/*G* barrier is just under half the values for the *F* and *C* sites (1.58 and 1.73 eV respectively).

A different entry to *G* is shown in Fig. 7(ii) where the Li atom enters the region by way of ring *E* and bond *e*. The minimum at *E* is insignificantly different from those in the rest of the molecule, such as are displayed in Fig. 7(i), but in order to traverse the exterior bond *e* on its journey to the *G* region the Li atom would have to overcome a barrier of 2.29 eV, or on a return route from *G* to *E* one of 1.14 eV. This contrasts sharply with the results discussed in the previous paragraph where exit and entry of the Li involved substantially lower barriers of 1.73 and 0.75 eV respectively.

The broken and dotted curves in Fig. 7(ii) describe the $C \rightarrow F \rightarrow G$ route discussed above when a second Li atom is located at one of the ring sites. The destabilization of one site by a second Li in a neighbouring site is similar to that in chrysene. Thus when the second Li is on ring *A* (broken curve), the minimum at *F*, and to progressively *smaller* extents the barrier at *C* and the *G* minimum, increase in energy with respect to the *C* site. Thus the raising of the *F* minimum by a Li atom at *A* (or *E*) facilitates migration into rings *C* (barrier reduced from 1.58 to 1.08 eV) or *G*(1.73 reduced to 1.48 eV). Similarly a Li atom at *B* (or *D*) raises the energies of, and the barrier between, sites *C* and *F* (dotted curve). Interestingly the energy of the site in *G* appears to be insensitive to the presence of a Li atom even as close as the site on *A*.

6. Discussion and conclusions

6.1. *Interdependence of sites*

Even if, as Bachrach and Streitwieser conclude [30] from their study of the basis sets of Li and C in small organolithium molecules, the basis set superposition error imposes an overestimation of the Mulliken population on the Li atom, the deviations which we find from $q_{\text{nett}} = +1$ warn of a possibly significant covalent contribution to the lattice energy. This emphasises the requirement of accurate (Li, C) potentials if the migration of the intercalant is to be investigated by lattice simulation methods. Our results also imply that despite the apparent covalency and the extensive electron delocalization, Li sites in neighbouring rings show little variation in binding energy - i.e. the C planes do not appear to mediate the presence of complexed atoms to other sites unless they are on adjacent rings (in which case those structures are usually destabilized). Since stoichiometry and structural investigations on first stage Li graphite render the occupation of such close sites unlikely it seems fair to conclude that intercalation of Li at one site is not greatly affected by the presence of Li atoms at non-adjacent ring sites, as far as static energy considerations are concerned. In a lattice simulation calculation it would therefore seem valid to assume independent atom-pair potential functions.

6.2. *Adjacent ring sites*

We turn next to the anomalous correlation calculated for two Li atoms on adjacent ring sites in pentacene as reported in Sect. 5.2 and illustrated by the deep energy well in the upper curve of Fig. 3. An examination of the LCAO coefficients of the Li hydrocarbon complexes shows *weak* mixing of the atomic orbitals (AOs) on the hydrocarbon and Li sublattices, and that the lithium atoms contribute mainly through their $2s$ and $2p_z$ orbitals. Although the MOs of the Li complexes are in essence either those of the hydrocarbon or of the Li sublattice the weak mixing reduces the energies of the Li-like MOs from those of the pure Li AOs, though usually not enough to be occupied by electrons. Thus in [chrysene. Li]$^+$ and [coronene.Li]$^+$, for example, the lowest unoccupied MO consists in each case of a dominant contribution from $2s$(Li) and $2p_z$(Li), a little from the Li $2p_x$ and $2p_y$ AOs and a slight admixture of hydrocarbon orbitals. In [pentacene.Li]$^+$, however, there exists a low energy unoccupied π MO which is nodeless over six *C* atoms - 4 of the Li-containing ring *E* and 4 of the adjacent ring *D*, including the two carbon atoms common to *D* and *E*. Such a MO is favourably disposed to interact with a Li atom over *D* at the same time permitting a bonding overlap between the two Li atoms on sites *D* and *E*. Consequently the energy level of this MO in [pentacene.Li$_2$]$^{2+}$ is lowered to a value which results in its becoming the highest occupied MO. Its occupation by an electron pair implies the formation of covalent bond between the Li atoms on the *D* and *E* sites whose separation (2.42 Å) is close to that (2.67 Å) of the Σ_g^+ ground state (26) of Li$_2$, and consequently results in *negative* charges on the Li atoms.

It is interesting that [pentacene.Li_2]$^{2+}$ with the lithium atoms complexed at D and E also contains a low-lying unoccupied MO which is favourable for interaction with a third lithium atom placed at C. In fact calculations similar to those described on [pentacene.Li_2]$^{2+}$ establish an extra stability for the complex [pentacene.Li_3]$^{3+}$ in which the Li atoms occupy the adjacent sites, C, D and E. Acenes thus appear to have the tendency to complex linear chains of Li atoms in their rings. Chains of alkali metal atoms have been detected in scattering experiments [31], and in fact Li_3 trapped on hydrocarbon matrices has been investigated by ESR [32].

On replacing pentacene by another aromatic hydrocarbon ahc there are no low-lying unoccupied MOs among the complexes [ahc.Li]$^+$ reported in section 5 which are favourable for interaction with a second Li atom, on a ring site adjacent to the first, to produce a comparably stable complexed Li_2 species such as we calculated in [pentacene.Li_2]$^{2+}$. It may be that the "favourable" MO in [acene.Li_n]$^{n+}$ is a consequence of the symmetry describing the straight acene chain and has no analogue in other symmetries.

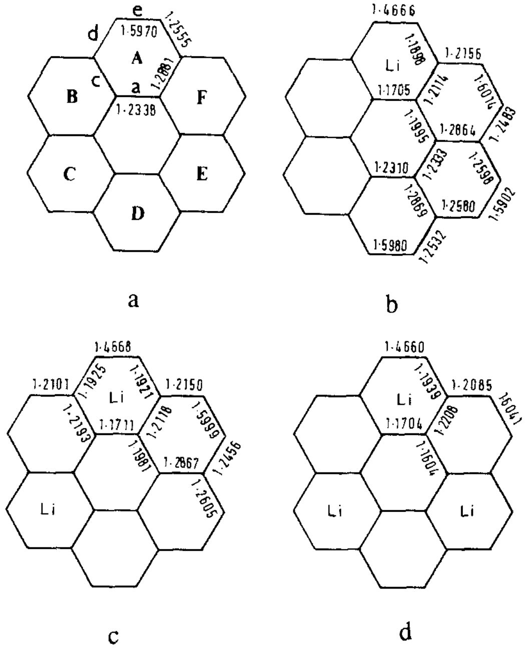
Wtih no current experimental data on the occlusion of Li atoms by polycyclic hydrocarbons to compare with the results reported in the previous two paragraphs, we may turn to the findings of electron spectroscopy and positron annihilation investigations of alkali metal graphite intercalates. Angle-resolved photoemission [33] and positron annihilation [9] studies on first-stage lithium intercalate agree with tight-binding and KKR muffin-tin calculations [34] on the same system in characterising a conduction band which is essentially a graphite π^* band, the calculations implying that the $2s$ band is well above the Fermi level. However electron spectroscopy [35] and positron annihilation studies [9] on C_8M intercalation compounds of K and heavier alkali metals exhibit conduction bands which are alkali-like s-type, the band structure calculations showing that in C_8K the lower part of the $4s$ band approaches the Fermi level more closely. These results are consistent with our own findings on Li aromatic hydrocarbon complexes, that the degree of mixing of Li and hydrocarbon orbitals is slight, and that consequently the energy of the Li-like MO is normally above that of the highest occupied MO. However the Li-like MO level is sensitive to small changes in the electronic structure of the complex, and it has been pointed out [9] that an appropriate amount of charge transfer from the metal to the carbons could even result in the lowering of the bottom of the conduction band of C_nM below the Fermi level. A similar event occurs in the [acene.Li_n]$^{n+}$ complexes discussed above.

6.3. Benzenoid character and complexing ability

At the end of Sect. 2.2 we decided to test whether those rings which the Clar rules [19] specified as fully benzenoid showed any difference in complexing power from those which contained π electrons localized in certain bonds which shared an "aromatic sextet" with other rings. The results described in Sect. 5.3 and 5.5 for chrysene and benzpyrene, two hydrocarbons containing fixed, fully benzenoid rings (*A*, *C* and *E* in both molecules) isolated by localized-electron bonds, showed rather uniform complexation energies and inter-ring barriers for the migration of a single Li atom over the surface. Moreover the small variation observed does not reflect the differences between the fully-benzenoid and non-benzenoid rings. It would therefore appear that whatever the shape of the edge of the *incident edge* of an aromatic plane upon which a Li atom enters the plane, the complexing and retaining power of the various rings is largely uniform.

The other possibility to be tested was whether, in molecules such as pentacene or coronene, whose symmetries preclude the localization of aromatic sextets to particular rings, a complexation of Li at a specific ring may fix sextets in other rings with the result that the other sites in the molecules, and by implication in the 2-dimensional carbon sublattice, are thereby determined. However since the remarks in the previous paragraph discount a correlation between fully benzenoid rings and extra-favourable complexation sites, this intriguing possibility must also be discounted.

However the complexation of lithium at ring sites does give rise to small effects which are in the direction specified in the Clar theory. We illustrate these for the complexation of coronene, although the other hydrocarbons show similar effects. We have already established that unlike benzperylene (IV) where the Wiberg bond orders in Fig. 1 showed that the removal of a ring from chrysene "fixes" Clar's three aromatic sextets in rings *A*, *C* and *E* (the equivalent of coronene's external rings), in III there is a sharing of three sextets between these rings. This should be reflected in the bond orders of III for, if each aromatic sextet is to be shared between two rings, bonds of type *e* (see Fig. 8a) would be expected to



a b

c d

Fig. 8. Wiberg bond orders of coronene (**a**), and when one, two or three Li atoms are complexed at the sites shown in (**b**), (**c**) and (**d**)

exhibit a bond order intermediate between that in a fully benzenoid ring and in an ethylene bond, while types *a* and *d* should be intermediate between a fully benzenoid bond and a bond with no π component. Thus bonds like *e* should be of high bond order, *a* and *d* of low order, while for bonds of type *c*, which remain benzenoid despite the sharing of the sextet, the bond order should be intermediate between the other two. All these predictions are confirmed by the Wiberg bond orders shown in Fig. 8a.

Also shown in Fig. 8 are the Wiberg bond orders in coronene resulting from the complexation of up to three Li atoms (ions). We test the possibility that complexation of Li at a given ring site fixes the aromatic sextet in that ring and thereby fixes the two other aromatic sextets in those rings predicted by the Clar rules. A comparison of the orders in (*a*) and (*b*) do indeed show that the bond order alternation in rings *C* and *E* decreases while that in rings *B*, *D* and *F* increases, just as would be expected if the complexed Li atom in *A* were to increase the benzenoid character of the ring. Similarly a comparison of the orders in the sequence (*b*) to (*d*) shows a progressive enhancement of these effects as more Li atoms are complexed.

It would therefore appear that, as monitored by bond orders, the complexation of Li does tend to render certain rings more benzene-like than others, and that these rings are the ones predicted by the Clar rules. However the effect is slight, and is not reflected in the energies of complexation, which appear to be largely independent of the presence of occupied ring sites.

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