

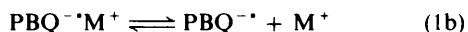
## An *Ab Initio* Molecular Orbital Study of the *p*-Benzoquinone Radical Anion and its Lithium Ketyl: Electronic Spectra and Intramolecular Cation Transfer in Ketyl Ion Pairs

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STO-3G SCF (unrestricted Hartree-Fock) molecular orbital calculations are described for the *p*-benzoquinone (PBQ) radical anion and the corresponding lithium ketyl. At equilibrium the lithium atom occupies one of two equivalent positions collinear with the carbonyl axes and 2.843 a.u. from the nearer oxygen atom. This planar structure contrasts with earlier predictions that the most stable position of the cation in ketyl ion pairs is above the plane of the anion; its significance in relation to the electronic spectra of ketyl ion pairs is examined. The potential surface generated by displacing Li with respect to PBQ is found and is used for discussion of the possible mechanism of intramolecular transfer of Li<sup>+</sup> between the two equivalent equilibrium sites. It is suggested that the rate-determining factor in this process is the formation of a solvent-shared ion pair and not (as has previously been assumed) the passage of the Li atom through the lowest saddle point on the contact ion pair potential surface.

Radical ions<sup>1</sup> are often paired with alkali- or alkaline earth-metal cations, and their physical and chemical behaviour is then profoundly influenced by the cation.<sup>1,2</sup> Despite the importance of such ions and ion pairs as precursors in organic synthesis and as reaction intermediates,<sup>3</sup> there has been relatively little theoretical study of them. In the present paper we therefore describe a low-level, *ab initio* molecular orbital study of the stable ions and ion pairs (ketyls) which are formed by reduction of *p*-benzoquinone (PBQ) by alkali-metals M in ethereal solvents [reactions (1)]. The results enable us to discuss the



Arrhenius parameters for an intramolecular rearrangement of the ion pair,<sup>4-7</sup> to comment further on the electronic spectra of ketyl ion pairs,<sup>8</sup> and, as is reported in a separate paper, to calculate the effect of solvent on ion pair properties.<sup>9</sup>

The free PBQ<sup>·-</sup> ion, sometimes observed in equilibrium with ion pairs, has the e.s.r. spectrum expected for four equivalent protons, implying that the two carbonyl groups in the free anion constitute equivalent binding sites.<sup>10,11</sup> There have been several e.s.r. studies of M<sup>+</sup>PBQ<sup>·-</sup>, with different M<sup>+</sup> and solvents,<sup>5,10,12,13</sup> and of alkyl-substituted derivatives of PBQ<sup>·-</sup>. Occurrence of M<sup>+</sup> hyperfine splittings provides direct evidence that M<sup>+</sup>PBQ<sup>·-</sup> ion pairs are of the 'tight' or contact type;<sup>14,15</sup> whilst a solvent-shared structure has been postulated for some radical ion pairs in order to account for the temperature-dependence of their absorption spectra, there is no evidence for solvent sharing in ketyl ion pairs at *equilibrium* geometry.<sup>7</sup> The decrease of the M<sup>+</sup> hyperfine splitting constant (h.f.s.c.) towards zero as the temperature is lowered probably indicates that M<sup>+</sup> is increasingly confined to a potential well in the nodal (molecular) plane;<sup>7,16</sup> the location of M<sup>+</sup> near to one CO group in the *static* ion pair is confirmed by <sup>17</sup>O, <sup>13</sup>C, and <sup>1</sup>H h.f.s.c.s, which show the inequivalence of the CO groups and of pairs of protons in the ion pair.<sup>12,13</sup>

Perhaps the most interesting e.s.r. observations are, however, those resulting from the migration of the cation between the two equivalent binding sites, which gives rise to characteristic e.s.r. spectra with alternative narrow and broad hyperfine lines when the rate of migration is comparable with the induced changes in the h.f.s.c.s.<sup>13,14</sup> The first-order rate constant for the migration

can be deduced from the change in linewidths with temperature and numerous experimental measurements of this type have been made.<sup>4-6,12</sup> Despite the extensive experimental data that exist on cation migration and the amount of discussion generated, the factors which determine the rate of the process on the whole remain obscure.

The SCF molecular orbital calculations on PBQ<sup>·-</sup> and Li<sup>+</sup>-PBQ<sup>·-</sup> in the gas phase, which we now describe, constitute the first step in a theoretical study of the problem. Such calculations are less easy for a radical ion pair than for the closed-shell ground state of a molecule of comparable size, partly because of the difficulty of locating the true ground configuration from the *aufbau* principle in the case of radicals, and partly because the ionicity of the wavefunction is sensitive to the balance of the alkali atomic basis set with the basis sets of other atoms. The size of the systems and the need for many trial computations thus restricted the present study to low-level calculations. Since very small split-valence-shell basis functions were not available for Li when this work was done, geometry optimizations were performed at STO-3G level, and, in addition, a few calculations with other bases were carried out for the optimized structures (see footnote† in *UHF calculations for Li-PBQ*).

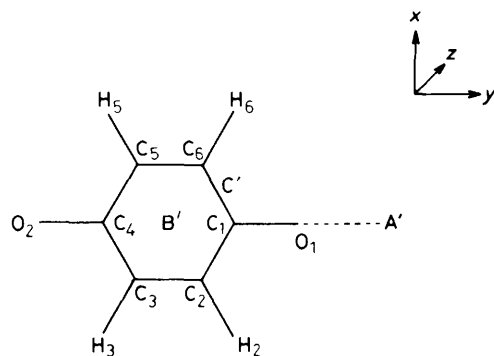
*UHF Calculations on PBQ<sup>·-</sup>.*—The *ab initio* LCAO-SCFMO wave functions were obtained at the STO-3G level using the unrestricted Hartree-Fock method and the GAUSSIAN 70 (ref. 17) and ATMOL3 (ref. 18) systems. The PBQ<sup>·-</sup> geometry was optimized, since this is not known experimentally. In calculations on the anion, *s,p*-constrained scale parameters optimized for the PBQ molecule at the experimental geometry<sup>19</sup> were used  $\zeta_{1sH} = 1.22$ ,  $\zeta_{1sC} = 5.70$ ,  $\zeta_{2s,pC} = 1.74$ ,  $\xi_{1sO} = 7.70$ ,  $\xi_{2s,pO} = 2.25$ ; these are similar to the standard values<sup>17</sup> (though optimization gives a reduction of 0.0123 a.u. in energy, leading to  $E = 374.3576$  a.u. for PBQ).

Geometry optimization of PBQ<sup>·-</sup> (*D*<sub>2h</sub> symmetry; see Figure and Table 1) produces a longer and narrower nuclear framework as compared with PBQ. The 'double bonds' are lengthened [with a 7% increase of  $r(\text{CO})$  similar to that found with H<sub>2</sub>CO<sup>·-</sup>] and the 'single' C(1)-C(2) bonds decrease slightly; the greatest change in bond angle is the 3° decrease of  $\angle \text{C}(6)\text{C}(1)\text{C}(2)$ . These changes are just what would be anticipated from simple Hückel molecular orbital theory when the unpaired electron enters the  $\pi^*$  lowest unoccupied orbital of PBQ. The atom populations of PBQ<sup>·-</sup> are also what one would

**Table 1.** Structure parameters for PBQ and  $\text{PBQ}^{\cdot-}$  (values in atomic units)

Parameters	PBQ <sup>a</sup>	PBQ <sup>b</sup>	PBQ <sup>c</sup>
$r[\text{C}(1)\text{-O}(1)]$	2.31	2.343	2.47
$r[\text{C}(1)\text{-C}(2)]$	2.78	2.776	2.72
$r[\text{C}(2)\text{-C}(3)]$	2.48	2.600	2.54
$r(\text{C-H})$	2.06 <sup>d</sup>	2.100	2.07
$\angle \text{C}(6)\text{C}(1)\text{C}(2)$ (°)	118	113.1	114.9
$\angle \text{C}(1)\text{C}(2)\text{C}(3)$ (°)	121	123.4	122.6
$\angle \text{C}(1)\text{C}(2)\text{H}$ (°)	119 <sup>d</sup>	118.5	117.5
$Q_{\text{O}^{\cdot}}$	-0.216		-0.302
$Q_{\text{C}(1)}$	0.194		0.038
$Q_{\text{C}(2)}$	-0.043		-0.090
$Q_{\text{H}}$	0.054		-0.027

<sup>a</sup> Geometrical parameters for the PBQ molecule are those derived experimentally (assuming  $D_{2h}$  symmetry); see ref. 19. <sup>b</sup> Values obtained (J. Spanget-Larson, *Theor. Chim. Acta*, 1978, **47**, 315) by MINDO/3-UHF treatment. <sup>c</sup> Values obtained in the present work. <sup>d</sup> Assumed. <sup>e</sup> The  $Q$  values are the Mulliken net atom charges obtained in the present work.



**Figure.**  $\text{PBQ}^{\cdot-}$  geometry. The centre of the six-membered ring is the origin of the Cartesian co-ordinates. Points A'—C' are the projections, in the (x,y) plane, of the Li atom positions defined in Table 2

expect from HMO theory (the HMO values for the corresponding hydrocarbon framework are equivalent to  $Q_{\text{O}} = -0.332$ ,  $Q_{\text{C}(1)} = -0.032$ , and  $Q_{\text{C}(2)} = -0.068$ ); however, the increase in the oxygen electron density in passing from PBQ to  $\text{PBQ}^{\cdot-}$  is much less pronounced than would be expected from HMO calculations. The geometry optimization produces an energy-lowering of 0.0283 a.u. to give  $E = -374.2826$  a.u. for the  ${}^2B_{3g}$  ground state of  $\text{PBQ}^{\cdot-}$ . Unfortunately, there is considerable higher-spin-state contamination of the UHF wavefunction, with  $\langle S^2 \rangle = 1.9$ .<sup>20-22</sup> The representation of  $\text{PBQ}^{\cdot-}$  is poor relative to PBQ; thus, the SCF estimate of the adiabatic electron affinity obtained here is  $-0.0750$  a.u. compared with the substantially exothermic\* experimental gas-phase value<sup>23</sup> of  $+0.0695$  a.u.

**UHF Calculations for Li-PBQ.**—An approximation introduced<sup>8</sup> in 1961 has been widely used for calculating ion pair properties; it consists of adding an electrostatic perturbation term due to the cation (which is treated as a point charge  $Z$  located at  $r_c$ , the centre of the cation) to the Hückel Hamiltonian. One then finds, for example, that the resulting

first-order change in electronic energy is given by equation (2)

$$E - E_0 = -Z \sum_{i=1}^N q_i / |r_i - r_c| \quad (2)$$

where  $q_i$  is the Hückel charge density at the  $i$ th atom, the centre of which is at  $r_i$ . On the whole, it seems that little improvement over this type of treatment is obtained by using more sophisticated  $\pi$ -electron treatments or the all-electron CNDO and INDO treatments;<sup>24-26</sup> the latter methods predict unreasonable ion pair geometries and there seems to be a tendency for the calculations to produce an incorrect homopolar configuration rather than an ionic ground state.

We are aware of only one previous *ab initio* SCF treatment of a chemically interesting radical ion pair, namely the UHF-STO-4G calculation for the pyrazine-Li complex<sup>27</sup> (see also ref. 28). This calculation showed the preferred location of Li to be in the nuclear plane along the N-N axis, which is consistent with experiment; as would be expected,<sup>21,29</sup> indifferent results were obtained for h.f.s.c.s calculated at the same time. Similar conclusions regarding the structure of the Li pyrazine complex have been reached by means of an 'electrostatic' (*ab initio* potential) calculation which has been applied to a number of large ion pair systems.<sup>20,26,30,31</sup> Unfortunately, because the latter calculation does not take the cation closed-shell explicitly into account (*cf.* ref. 26) it cannot in general be expected to yield reliable geometries.

We performed UHF calculations on Li-PBQ using the geometry and LCAO basis described above for  $\text{PBQ}^{\cdot-}$ , augmented by  $1s$  ( $\zeta = 2.69$ ) and  $2s, 2p$  ( $\zeta = 0.80$ ) for Li. A scan of the potential surface using GAUSSIAN 70, followed by detailed optimization, showed that there are three structural configurations of interest, A—C (Table 2).<sup>†</sup> As in the case of the lithium-formaldehyde ketyl,<sup>28</sup> the predicted equilibrium location of the Li (A) is in the nuclear plane collinear with the C—O bond at a distance 2.84 a.u. from the nearer oxygen. There is also a potential well over the centre of the ring, so a second  $C_{2v}$  conformer (B) is predicted with an optimum distance above the ring of 3 a.u. Conformer B is considerably less (0.0708 a.u.) stable than A. The third configuration<sup>‡</sup> C represents the transition state for the exchange of Li between the two equivalent binding sites (A). The reaction path through C is the

<sup>†</sup> Calculations with other bases were also carried out for these structures. For STO-6G (*s,p*-constrained) the relative energies are  $E(\text{C}) - E(\text{A}) = 0.1002$ ,  $E(\text{C}) - E(\text{B}) = 0.0317$  a.u. These are closely similar to the STO-3G values of 0.1023 and 0.0315 a.u., respectively; the 6G and 3G calculations also gave very similar orbital populations, *etc.* Using best atom (*s,p*-unconstrained) STO-3G the relative energies are  $E(\text{C}) - E(\text{A}) = 0.0717$  and  $E(\text{C}) - E(\text{A}) = 0.0027$  a.u.

<sup>‡</sup> Since, in the UHF treatment, there are frequently several electronic configurations with near-ground-state energies, it is well known that constructing the trial wavefunction using the *aufbau* principle does not guarantee convergence to the true ground state. We therefore used ATMOL3 to explore (by a limited amount of orbital swapping) the reliability of our GAUSSIAN 70 results. In the case of A and B we did not find states of lower energy than those previously obtained; however, in case C we found that by swapping the lowest  $\alpha$ -virtual MO with the highest  $\alpha$ -occupied MO there is obtained an electronic state which has an energy lower (by 0.0297 a.u.) than that described in Table 2. It seems that this new state can best be described as a repulsive interaction between Li and PBQ; the unpaired electron MO consists mainly of Li  $s$  and  $2p_z$  atomic orbitals with  $2s$  and  $2p_z$  combined so as to direct the electron away from PBQ beyond the Li nucleus. The most extraordinary feature of this new electronic configuration, which suffers from extremely bad spin-contamination, is the effect of quartet annihilation, which causes  $\langle S^2 \rangle$  to increase from 2.48 to 4.32! Thus the higher multiplets (sextet, octet, *etc.*) are the major spin contaminants rather than the quartet; presumably the poor basis set is the underlying reason for this.

\* Despite this exothermic value, PBQ does not capture thermal electrons, which is consistent with the prediction of a structurally different anion, implying poor overlap between the vibrational wavefunctions of PBQ and  $\text{PBQ}^{\cdot-}$ .

most favourable route if a contact ion pair structure is maintained throughout; in particular all structures in which Li is located in the nuclear plane away from the equilibrium positions have too high an energy to be physically important.\* The calculated energy of C is large relative to the energy of the equilibrium structure; we discuss the implications of this later.

*Effect of the Cation on the Electronic Spectrum of a Contact Ion Pair.*—Calculations of electronic energy,<sup>8,26</sup> for alkali aromatic hydrocarbon ion pairs using equation (2) or a full Hückel calculation lead to the conclusion that the equilibrium ion pair structures are similar to B in Table 2, i.e. that the cation lies in a plane parallel to the plane of the anion and above its symmetry centre; a similar result is found for the benzophenone ketyls,<sup>8</sup> the equilibrium position being in the symmetry plane of the ketone above the C=O bond. On the other hand, our *ab initio* calculations for Li<sup>+</sup>PBQ<sup>-</sup> show the planar structure A to be more stable, and this result will, presumably be found in other cases.<sup>27,28</sup> Our 1961 analysis<sup>8</sup> of the ketyl ion pair spectra therefore requires the following slight modification to accommodate the possibility of this structure.

The denominators in equation (2) may be expanded about any point *P* (at  $r_p$ ) which satisfies equations (3). Thus, we have

$$|r_i - r_p| = \rho_i \quad (3a)$$

$$|r_c - r_p| = r_o \quad (3b)$$

$$r_o > \rho_i \quad (3c)$$

$$E - E_o = \frac{1}{r_o} \sum_{i=1}^N q_i + \frac{1}{r_o^2} \sum_{i=1}^N q_i \rho_i \cos \theta_i + \frac{1}{r_o} \sum_{i=1}^N \sum_{l=2}^{\infty} \left(\frac{\rho_i}{r_o}\right)^l P_l(\cos \theta_i) \quad (4)$$

equation (4) where  $\theta_i$  is the angle between  $(r_i - r_p)$  and  $(r_c - r_p)$ , and  $P_l$  is a Legendre polynomial.

If  $\Delta E$  and  $\Delta E_o$  are the changes in  $E$  and  $E_o$  when the anion is excited to a higher electronic state, and  $\Delta q_i$  is the associated change in electron density at the  $i$ th atom, application of equation (4) to the ground and excited states leads to (5), the

$$\Delta E - \Delta E_o = \frac{1}{r_o} \sum_{i=1}^N \Delta q_i \cos \theta_i + 0 \left(\frac{1}{r_o^3}\right) + \dots \quad (5)$$

term in  $1/r_o$  vanishing because the total charge is conserved. For the planar ion pair structure we may, as an approximation, retain only the first term on the right-hand side of equation (5), i.e., where  $\Delta\mu^{\parallel}$  is the increase in the component of the dipole

$$\Delta E - \Delta E_o = \frac{\Delta\mu^{\parallel}}{r_o^2} + \dots \quad (6)$$

moment of the anion in the direction of  $(r_c - r_p)$ , upon electronic excitation. The best quadratic approximation of this type is obtained by choosing  $r_p$  so as to maximize the first right-

hand-side term of equation (5), i.e. to minimize  $r_o$  subject to condition (3c). In the case of alkali-PBQ or alkali-benzophenone ion pairs with the cation collinear with the C=O group, the optimum position of *P* is on the C=O axis *ca.* 1 a.u. from the C atom on the side remote from O. A somewhat different analysis is needed for the out-of-plane equilibrium position of the cation, and it is then found<sup>8</sup> that the appropriate quadratic approximation is (7) where  $r_o$  is the perpendicular distance of the centre of the cation from the plane of the anion.

$$\Delta E - \Delta E_o = \frac{0.293}{r_o^2} \sum_{i=1}^N \rho_i \Delta q_i \quad (7)$$

The present discussion reinforces our previous argument<sup>8</sup> that the spectral shift caused by the cation (i.e.  $\Delta E - \Delta E_o$ ) is a linear function of the square of the cation-anion distance. To obtain an estimate of this distance, the radius  $R_c$  of a cation  $M^+$  is taken to be the van der Waals radius of the inert gas which is isoelectronic with  $M^+$ ; the radius of an atom in the anion is taken to be the van der Waals radius of the neon atom. Thus, in rounded values,  $r_o = R_c + \beta$ , where  $\beta = 2$  a.u. if the centre of the cation lies above the plane of the anion, and  $\beta = 5.5$  a.u. if the cation is collinear with the C=O group. In some circumstances the electronic spectra of ketyls may be complicated by the presence of ion aggregates of various kinds. These complications are, however, unimportant in the case of the alkali-metal-benzophenone ketyls in dioxane solution; for these species the absorption spectrum in the visible region consists of a single band without evidence of shoulders or asymmetry, and Beer's law is obeyed accurately.<sup>32</sup> Hence Table 2 shows the values of  $\nu_o$  and  $\alpha$ , obtained by least-squares fit of frequencies  $\nu$  for alkali-metal-benzophenone ion pairs in dioxane solution to the expression (8).

$$\nu = \nu_o + \alpha/(R_c + \beta)^2 \quad (8)$$

The linearity is good in all cases; numerical tests show that uncertainties of 0.1 a.u. in  $R_c$  values and 100  $\text{cm}^{-1}$  in  $\nu$  values can change the correlation coefficient  $\gamma$  by up to 0.02, so that values of  $\gamma$  in the range  $0.98 \leq \gamma \leq 1$  are regarded as implying satisfactory agreement of the data with equation (8). To obtain theoretical estimates of the parameter  $\alpha$  from equations (6) and (7) we use the Hückel-topological molecular orbitals described in ref. 33. Thus, with the notation of ref. 33, we consider two excited energy levels, one associated with an orbital designated as  $G_{-+}$ , the other (degenerate) from  $G_{--}$  or  $G_{+-}$ . The values of  $\alpha$  (a.u.) calculated from the corresponding Hückel values of  $\Delta q_i$  are:

from equation (6) (planar ion pair):

$$\alpha = \Delta\mu^{\parallel} = 2.37 (G_{-+}) \text{ or } 2.21 (G_{--})$$

from equation (7) (non-planar ion pair):

$$\alpha = 0.293 \sum_{i=1}^N \rho_i \Delta q_i = 2.08 (G_{-+}) \text{ or } 1.77 (G_{--})$$

Agreement between these values and those in Table 3 is particularly good when the larger  $\beta$  values are used, and it is tempting to interpret this as indicating planar ion pair structures in which the effective inter-ionic distance is *ca.* 1 Å greater than the van der Waals value because of solvation; more accurate calculations would be required to substantiate this, however.

*Arrhenius Parameters for Intramolecular Cation Transfer.*—In general the rate of intramolecular cation migration (in a given solvent) increases with increasing cation size.<sup>4,5,6,12</sup> It is

\* It is of some theoretical interest that GAUSSIAN 70 converges to different electronic configurations for different areas of the plane. Thus, in the Figure, the positive quadrant is divided into two regions roughly by projection of the line joining C(4) and H(2). For Li positions on the O(1) side of this imaginary line convergence is to a  $\pi$ -radical ( $^2A'$ ) state with a significant positive  $Q_{Li}$  (of *ca.* 0.4), whereas within the other region a  $\sigma$ -radical ( $^2A'$ ) state with  $Q_{Li}$  *ca.* 0.05 is obtained. Either the computations have failed to produce the true ground state in the  $^2A'$  case, or the potential surfaces of the two states cross (constituting a breakdown of the Born-Openheimer principle).

Table 2. Ion pair configurations of interest

Configuration	A	B	C
State	${}^2B_1$	${}^2B_1$	${}^2A$
Energy (a.u.)	-381.8304	-381.7596	-381.7281
Co-ordinates of Li (a.u.)			
x	0	0	1.091
y	8.047	0	2.336
z	0	3.00	3.500

Table 3. Dependence on cation radius of absorption spectra of alkali-metal benzophenone ion pairs in dioxane solution<sup>a</sup>

$\beta$ /a.u.	$\nu_0/1000\text{ cm}^{-1}$	$\alpha$ /a.u.	$\gamma$
2	13.4	0.17	0.994
2.5	13.2	0.23	0.993
5.5	12.0	0.95	0.987
6	11.9	1.14	0.986
8	11.1	2.13	0.984

<sup>a</sup> The constants  $\alpha$ ,  $\beta$ , and  $\nu_0$  are those in equation (8);  $\gamma$  is the correlation coefficient. Experimental data are from ref. 32.

reasonable to suppose that the trend has its origin in the weakening of the cation perturbation as the inter-ionic distance increases, and confirmation of this is found in the linear relationship between the cation perturbation (as measured by the h.s.f.c.s of the methyl protons), and the Gibbs free energy  $\Delta G^\ddagger$  for the rate process.<sup>12</sup> For a wide range of anions,<sup>4,5,6,12</sup> alkali-metal cations and solvents, the values of  $\Delta H^\ddagger$  are mostly between 12 and 30 kJ mol<sup>-1</sup>. The Arrhenius pre-exponential factor is typically low (ca.  $10^{10}\text{ s}^{-1}$ ), corresponding to a substantially negative (ca.  $-80\text{ J K}^{-1}\text{ mol}^{-1}$ ) value of  $\Delta S^\ddagger$ . Theoretical estimates of  $\Delta H^\ddagger$  have been obtained by means of several molecular orbital and electrostatic approximations for contact ion pairs, seemingly with some success.<sup>20,26,30</sup> Ours is, however, apparently the first *ab initio* calculation of  $\Delta H^\ddagger$  and, as we have seen earlier, it leads to  $\Delta H^\ddagger = 0.1023\text{ a.u.} = 268.5\text{ kJ mol}^{-1}$ . The discrepancy between this and the range of experimental values seems too large to be explained in terms of the inadequacy of the basis set<sup>34</sup> or the enthalpies of solvation of contact ion pairs.\*

The most reasonable inference from this result is that the contact ion pair model does not provide a good starting point for calculating  $\Delta H^\ddagger$ , i.e. the usual description of the rate process in terms of the contact ion pair potential surface does not apply in the case of  $\text{Li}^+\text{PBQ}^{2-}$  (and thus probably in other cases also). A more appropriate description of the activation process seems to be the formation of a solvent-shared ion pair,<sup>35</sup> i.e., the insertion of a solvent molecule between the cation and anion which thereby increases the cation-anion distance by, typically, 10 a.u. At such large cation-anion distances the electronic energy of the anion is almost independent of its orientation with respect to the cation. The contact ion pair potential surface is

\* Estimates of the effect of solvation on  $\Delta H^\ddagger$  were made in various ways: (i) by considering the effect on the energy of the anion of three solvent dipoles tetrahedrally bound to the  $\text{Li}^+$  cation, (ii) by treating the ion pair as a point dipole in a spherical cavity in a dielectric continuum and, (iii) by a more complete ion-in-continuum calculation.<sup>9</sup> In each case the contribution of solvation to  $\Delta H^\ddagger$  was of the order of 0.001–0.01 a.u.

† To make the comparison with the  $\text{Li}^+\text{Fl}^-$  calculation as close as possible, the net charges of the H atoms in  $\text{PBQ}^{2-}$  were combined with those on the adjacent C atoms.

then largely irrelevant to  $\Delta H^\ddagger$ ; instead, we may write  $\Delta H^\ddagger = E_i$  where  $E_i$  is the energy of insertion of a solvent molecule between the cation and anion in solution.  $E_i$  is essentially the difference between two large terms, i.e.,  $E_i \approx E_s + E_1$  where  $E_1 (>0)$  is the energy required *in vacuo* to increase the inter-ionic distance from the contact ion pair value to the solvent-separated ion pair value, and  $E_s (<0)$  is the increase in ion pair-solvent interaction energy when the contact ion pair changes to the solvent-separated ion pair; the predominant contribution to  $E_s$  is the *in vacuo* energy of interaction of the inserted solvent molecule with the cation and anion. The delicate balance between  $E_s$  and  $E_1$  is demonstrated in those cases for which the equilibrium between solvent-separated and contact ion pairs has been studied. (See, e.g. refs. 35–37.) Thus, for lithium fluorenyl ( $\text{Li}^+\text{Fl}^-$ ) in tetrahydrofuran solution,<sup>35</sup>  $E_i \approx -29\text{ kJ mol}^{-1}$ . We made an order-of-magnitude estimate † (denoted by  $E'_i$ ) of  $E_1$  by applying equation (2) to the model and charge distribution of  $\text{Li}^+\text{Fl}^-$  described in ref. 36, with  $\text{Li}^+$  3 a.u. above the centre of the five-membered ring. This calculation gives  $E'_i = 0.122\text{ a.u.} = 320\text{ kJ mol}^{-1}$ , and, in view of the value of  $E_i$ , it is apparent that  $E_s$  must have the same order of magnitude as this. A corresponding calculation for the planar structure of  $\text{Li}^+\text{PBQ}^-$  gives the almost identical results  $E'_i = 0.120\text{ a.u.}$  The most important contribution to  $E_s$  is from the interaction of the inserted solvent molecule with the cation and we thus expect  $E_s$  to have similar values for  $\text{Li}^+\text{Fl}^-$  and  $\text{Li}^+\text{PBQ}^{2-}$ . However, formation of solvent-shared ion pairs of the ketyls is apparently unknown, which suggests that  $E_i$  is less negative for the ketyls than for the fluorenyls. The difference in  $E_i$  for  $\text{Li}^+\text{Fl}^-$  and  $\text{Li}^+\text{PBQ}^{2-}$  is, in view of the foregoing discussion, attributable mainly to differences in polarization-stabilization in the two cases. Thus, the polarization of the anion by the cation will be greater for the planar  $\text{Li}^+\text{PBQ}^{2-}$  structure than for the  $\text{Li}^+\text{Fl}^-$  structure in which  $\text{Li}^+$  lies above the centre of  $\text{Fl}^-$ . To account for the observed order of magnitude of  $\Delta H^\ddagger$  on this basis the polarization-stabilization of the equilibrium contact ion pair structure would need to be ca. 0.02 a.u. greater for  $\text{Li}^+\text{PBQ}^-$  than for  $\text{Li}^+\text{Fl}^-$ , and this seems eminently reasonable. In a corresponding way the entropy of activation can be identified with  $\Delta S_i$ , the entropy of formation of a solvent-shared ion pair from a contact ion pair. Typical values<sup>35,37</sup> of  $\Delta S_i$  are ca.  $-100\text{ J K}^{-1}\text{ mol}^{-1}$ , in keeping with the observed  $\Delta S^\ddagger$  values described above.

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