

## Mixed valence/dipole-bound dianions

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The possibility of binding two electrons to a molecule utilizing two distinct electron binding sites (i.e., one valence- and one dipole-binding center) is studied using *ab initio* electronic structure methods. It is found that if the electron binding energy of the dipole-binding site is large enough to overcome the Coulomb repulsion produced by the valence-bound electron, the dianion can be electronically stable with respect to the corresponding monoanion. It is also found that, for reasonable dipole- and valence-binding strengths, the separation between the two sites can be small enough to render the species within the current realm of synthetic possibility. Numerical results are presented for the dianions of  $\text{LiCN}\cdot\cdot\text{LiCC-PF}_5$  and  $\text{LiCN}\cdot\cdot\text{LiCN}\cdot\cdot\text{LiCC-PF}_5$ , whose vertical electronic stabilities are 0.120 and 0.808 eV, and whose stabilities with respect to fragmentation (i.e., loss of  $\text{LiCN}^-$ ) are 3.9 and 36.5 kcal/mol [including zero point energy (ZPE)], respectively.  
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### I. INTRODUCTION

It was recognized long ago that dipole-bound singly charged anions can be electronically stable if the dipole moment  $\mu$  of the neutral molecular host exceeds 1.625 Debyes (D).<sup>1</sup> Specifically with dipole moments greater than this critical value, for a point dipole potential ( $V = -\mu e \cos \theta / r^2$ ), there is an infinity of bound states within the context of the Born-Oppenheimer (BO) approximation (i.e., when the dipole is not rotating or vibrating). Jordan and Luken demonstrated that the loosely bound electron in a dipole-bound state occupies a diffuse orbital localized mainly on the positive side of the molecular dipole<sup>2</sup> and that the presence of inner shell electrons likely increases the critical dipole moment to at least 2 D to achieve an experimentally significant binding (e.g., of at least a few  $\text{cm}^{-1}$ ). The role of non-BO coupling was studied by Garrett, who concluded that such couplings are negligible for dipole-bound states with electron binding energies ( $E$ ) much larger than molecular rotational constants.<sup>3</sup> Finally, we earlier demonstrated for a number of systems<sup>4-12</sup> that correlated calculations are required in order to obtain correct values of  $E$  even though the weakly bound electron resides far from the molecular framework in a diffuse orbital.

As far as multiply charged anions are concerned, the attention of experimentalists and computational chemists who deal with them has been limited so far to valence-bound species.<sup>13-17</sup> Many valence-bound dianions that are very well known in condensed phases (e.g.,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ) are found to be electronically unstable in the gas phase because of the

strong Coulomb repulsion between the two excess electrons.<sup>17</sup> Most valence multiply charged anions that are stable in the gas phase overcome this repulsion by localizing the excess negative charges at two spatially separated sites (e.g., as in  $^-\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2^-$  or in  $^-\text{O}_3\text{S}-\text{O}-\text{O}-\text{SO}_3^-$ ) or delocalizing the charges among several electronegative atoms<sup>18,19</sup> (e.g., in  $\text{TeF}_8^{2-}$ ).

Recently, we studied the possibility of binding two electrons to a fixed finite dipole<sup>20</sup> and showed computationally that the critical value of the dipole moment  $\mu = qR$  required to bind two electrons seems to approach a value below 2 D in the ‘‘point-dipole’’ limit of large  $q$  and small  $R$ . Moreover, we showed analytically that, in the point-dipole limit, the critical dipole value does indeed approach that for binding a single electron (1.625 D). However, we concluded that it would be difficult to find a real molecule that can bind two electrons via its dipole potential (because the extent of polarity and/or the length of the molecule would be unrealistically large).

We also described very recently the possibilities of binding of an extra electron by a molecule possessing oppositely directed two polar ends (e.g.,  $\text{LiCN}\cdot\cdot\text{HCCH}\cdot\cdot\text{NCLi}$ ) but no net dipole moment.<sup>21</sup> Although such systems have zero dipole moment and large quadrupole moment, we showed that it is better to view the extra electron as dipole-bound rather than quadrupole-bound. That is, we consider the extra electron as being bound by the potential produced by the two local dipoles oriented in opposite directions. In addition, we anticipated that there is a real chance to find systems which can bind two excess electrons by such pairs of spatially separated dipole potentials.

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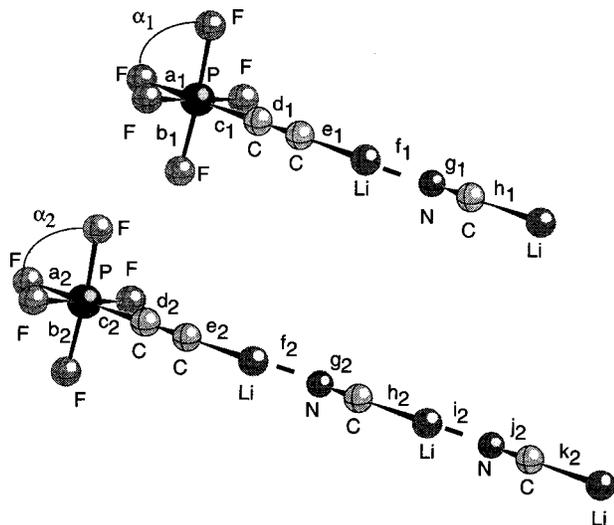


FIG. 1. Equilibrium structures of the dianions of  $\text{LiCN}\cdot\text{LiCC-PF}_5$  (top) and  $\text{LiCN}\cdot\text{LiCN}\cdot\text{LiCC-PF}_5$  (bottom) and the definition of geometrical parameters.

Although binding of two electrons to a single dipole site may be improbable, it may be possible to form a mixed valence/dipole-bound dianion of a polar molecule, with one excess electron dipole-bound and localized on the positive side of the molecular dipole, and the second excess electron bound by valence interactions to another functional group at a distant part of a molecule. In this work, we report our numerical results for two such molecules,  $\text{LiCN}\cdot\text{LiCC-PF}_5$  and  $\text{LiCN}\cdot\text{LiCN}\cdot\text{LiCC-PF}_5$  (see Fig. 1), which our findings suggest can bind two electrons in the manner just described. We also discuss the conditions that must be fulfilled by candidate molecules if such mixed valence/dipole-bound dianions are to be formed.

## II. METHODS

The equilibrium geometries of the neutral  $(\text{LiCN})_n\cdot\text{LiCC-PF}_5$  ( $n=1-2$ ) molecules and their anionic and dianionic daughters have been optimized and their harmonic vibrational frequencies have been calculated at the unrestricted self-consistent field (SCF) level (which is important to use for the open-shell systems). In these calculations, the values of  $\langle S^2 \rangle$  never exceeded 0.7501, 2.0005, and 3.7505 for the doublet, triplet, and quartet states, respectively, so we are confident that spin-contamination effects are not serious. The electronic stabilities of the mono- and dianions were calculated using the perturbation scheme described in Ref. 7, which generates Koopmans' theorem (KT),<sup>22</sup> SCF-difference ( $\Delta\text{SCF}$ ), and Møller-Plesset difference (MPn) values of the binding energies. Since the systems studied contain up to 15 heavy atoms, we had to limit the level of our calculations to the second-order MP2 level of perturbation theory for the larger species. However, it was possible to undertake coupled-cluster calculations with single and double excitations (CCSD) for the smaller system, which was important since the MP2 results were not conclusive in this case. All calculations were performed with the

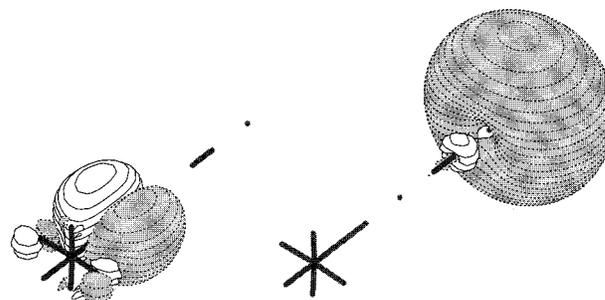


FIG. 2. The molecular orbitals of the  $(\text{LiCN}\cdot\text{LiCC-PF}_5)^{2-}$  dianion describing two excess electrons: valence-bound (doubly occupied, degenerate) orbital—left, and dipole-bound (singly occupied) orbital—right.

GAUSSIAN 98 program<sup>23</sup> and the three-dimensional plots of molecular orbitals were generated with the MOLDEEN program.<sup>24</sup>

The choice of the atomic orbital basis set used to describe the neutral molecule and the excess valence-bound electron is very important for reproducing the correct value of the electron binding energy. The basis set should be flexible enough to: (i) describe the static charge distribution of the neutral molecular host, and (ii) allow for polarization and dispersion stabilization of the anions upon electron attachment. For these purposes, we used the aug-cc-pVDZ basis set<sup>25</sup> based on our recent study on the influence of the basis set on the electron binding energies of molecular anions.<sup>26</sup>

On the other hand, the diffuse character of the orbital describing the excess dipole-bound electron (see Fig. 2) necessitates the addition of extra diffuse functions having very low exponents.<sup>8</sup> Hence, we supplemented the aug-cc-pVDZ basis set with extra even-tempered four-term  $s$  and four-term  $p$  sets of diffuse functions centered on the terminal lithium atom (since this is the positive end of the dipole). The extra diffuse  $s$  and  $p$  functions do not share exponent values. The geometric progression ratio was equal to 3.2,<sup>27</sup> and, for every symmetry, we started to build up the exponents from the lowest exponent of the same symmetry included in the aug-cc-pVDZ basis set designed for lithium. As a consequence, we achieved lowest exponents of  $8.239\,746 \times 10^{-5}$  and  $5.521\,774 \times 10^{-5}$  for  $s$  and  $p$  symmetries, respectively.

## III. RESULTS

An extensive search for mixed valence/dipole-bound dianions (detailed further below) led us to two species  $(\text{LiCN}\cdot\text{LiCC-PF}_5)^{2-}$  and  $(\text{LiCN}\cdot\text{LiCN}\cdot\text{LiCC-PF}_5)^{2-}$  which we determined can indeed form such dianionic states and for which we present detailed findings below in Sec. III B. One electron in both cases is valence-bound on the  $\text{CC-PF}_5$  terminus and the second (dipole-bound) electron is bound by 0.120 and 0.808 eV, for  $n=1$  and 2, respectively, to the Li end of the molecule. Before we discuss the detailed results for these two dianions, we want to explain the search that culminated in this pair of candidates for mixed valence/dipole binding because what we discovered in this search will likely be useful to others who examine such dianions.

## A. Strategy for designing mixed valence/dipole-bound species

It should be obvious that a dianion with its two centers of excess charge spatially separated by a distance  $r$  may be electronically stable if the Coulomb repulsion ( $1/r$  in atomic units) between the two extra electrons is overcome. Hence, we focused our efforts on linear or quasilinear species for which  $1/r$  could be easily estimated (i.e., having clearly identified binding sites). Because the dipole binding potential is known to usually produce weak binding, the  $1/r$  repulsion will be less than this binding only for long systems, so we anticipated having to construct long linear molecules as candidates, but we also tried to use highly polar "building blocks" to allow the dipole-binding site to be strong so that  $r$  would not have to be unrealistically large.

### 1. Covalently connected spacers

With these ideas in mind, we first considered (the valence binding site is on the right in all cases) the following neutral molecules: H-CC-CC-CC-O, Li-CC-CC-CC-O, Li-CC-CC-CC-S, and Li-CC-CC-CC-CC, but none was able to bind two electrons at the KT level (this, of course, does not prove they cannot bind when electron correlation is included, but we took this evidence as not encouraging). Moreover, we found that the destabilization of the dipole-bound electron caused by the presence of the valence-bound electron a distance  $r$  away [determined by the length of the spacer (-CC-) $_n$  groups] was even greater than expected from the  $1/r$  formula. In particular, the (-CC-) $_n$  spacer did not act to dielectrically screen the Coulomb repulsion of the two excess electrons. Instead, the more tightly valence-bound anion center induced electronic polarization within the spacer that acted to destabilize the dipolar electron binding center.

### 2. Noncovalently connected spacers based on HCN

Therefore, we decided to next examine systems in which the electronic polarization of the spacer is limited by the presence of intervening hydrogen bonds (i.e., spacers containing hydrogen bonds rather than quite polarizable covalent bonds). We found that the LiCN $\cdots$ (HCN) $_n\cdots$ H-CC systems with  $n > 1$  (N.B., these species possess one unpaired electron at the H-CC terminus), at the equilibrium geometry of the singlet monoanion, produced dianions (which have one electron on the Li end and two singlet-paired electrons on the H-CC group) that are electronically stable with respect to the closed-shell *singlet* states of the corresponding monoanions (with no electron on the Li end and two on the H-CC). In particular, the vertical attachment energies calculated at the KT level with the aug-cc-pVDZ+5s5p basis set were equal to 0.162, 0.386, and 0.533 eV, for  $n=2, 3$  and 4, respectively. However, geometry optimization of the dianion produced Coulomb explosion into H-CC $^-$  and  $^-$ LiCN $\cdots$ (HCN) $_n$ . That is, these dianions are not geometrically stable because the Coulomb repulsion is too strong for the hydrogen bonds that hold the neutral and monoanion together. This (failed) experiment did, however, show us that polarization of the hydrogen-bond spacer was marginal, so

polarization of the spacer did not destabilize the dipolar electron binding center beyond that contained in  $1/r$ .

### 3. Testing the Coulomb model

We next decided to carry out a series of model calculations designed to determine whether the dianion detachment energy could be estimated (at least at the KT level) by the simple formula

$$E^{\text{KT}}(\text{dianion}) = E^{\text{KT}}(\text{monoanion}) - \frac{1}{r}. \quad (1)$$

In the above formula,  $E^{\text{KT}}(\text{dianion})$  indicates the electron binding energy of the dianion and  $E^{\text{KT}}(\text{monoanion})$  indicates the electron binding energy of the dipole-bound monoanion (both calculated at the KT level), while  $r$  is the spacer length. In particular, we wanted to determine to what extent this estimate remains valid, even when the two electron binding sites are separated by spacers that can be strongly polarized.

First, we examined the linear HCN tetramer for which the electron binding energy in the dipole-bound monoanion [ $E^{\text{KT}}(\text{monoanion})$ ] is known to be 1762 cm $^{-1}$ .<sup>12</sup> The length of this molecule is taken to be 15.25 Å (its H to terminal-N distance). We then placed an F $^-$  anion a distance  $L$  from the terminal N atom, so the distance  $r$  between the hydrogen at the positive end of the dipole and the F $^-$  anion (i.e., the valence binding center) is  $r = L + 15.25$  Å. We computed the vertical electronic stability of such a dianion at the KT level and found that the smallest distance  $r$  that allows the dianion to remain stable is 75.75 Å (i.e., for  $r < 75$  Å, the second electron did not bind to the Li center). In comparison, the critical distance  $r$  that results from the above formula [using the KT stability of the isolated dipole bound (HCN) $_4^-$  monoanion and the  $1/r$  estimate of the Coulomb repulsion] is found to be 78.75 Å, which is quite close to what we find in the *ab initio* calculation. Moreover, the electrostatic formula also works for longer distances  $r$  in predicting the dianion's binding energy (i.e., in the region where the dianion is stable). We therefore conclude that the electrostatic estimate of the critical distance ( $r$ ) between two anionic centers can be used in designing real mixed valence/dipole-bound dianions.

### 4. Systems where the dipole and valence binding sites are not well matched

Next, we decided to focus on using LiCN rather than HCN as a "building block" because the former's much larger dipole moment gives rise to much stronger electron binding. In particular, we began by exploring species containing (LiCN) $_n$  clusters because: (i) the neutral dimer possesses a large dipole moment (21.2 D) and binds an electron by 1.346 eV at the KT level, and (ii) the interfragment structure of (LiCN) $_n$  should be more rigid than in (HCN) $_n$  due to the stronger N $\cdots$ Li bonds and thus may be strong enough to resist Coulomb explosion. Using the electrostatic model described previously and assuming a length for (LiCN) $_2$  of 8.30 Å, we performed calculations for the linear (LiCN) $_2\cdots$ LiCC that possesses a valence hole at the Li-CC

site (because we found that H-CC binds an electron by 3.490 eV, we thought Li-CC would be a good candidate for the valence binding site). This system was anticipated to bind an excess electron via its dipole potential at least as tightly as does (LiCN)<sub>2</sub>, and to be long enough ( $r$  is ca. 13.5 Å) to be a good candidate to form a stable dianion according to our electrostatic estimate.

The neutral open-shell LiCN··LiCN··LiCC possesses one unpaired electron (on the Li-CC group) and has a doublet state. The first extra electron added to the neutral system was expected to be strongly valence bound and to produce a closed-shell valence monoanion (having two electrons on its Li-CC terminus) in a singlet state. However, these expectations were not realized, and the first extra electron was observed to bind instead to the Li site. As a result, the monoanion's open-shell triplet state, with the extra electron on the Li site and a hole on the Li-CC site, is the lowest energy state. The corresponding open-shell singlet state is 0.490 eV higher and the (anticipated) closed-shell singlet state (with two electrons on the Li-CC site) lies 2.428 eV above this triplet. In essence, the very large dipole moment of LiCN··LiCN··LiCC causes the Li site on the left terminus to bind an electron even more strongly than does the Li-CC valence site, thus causing the open-shell states to lie below the closed-shell singlet.

When we then attempted to add a second extra electron to LiCN··LiCN··LiCC to form the dianion, we found the dianion to be stable with respect to the closed-shell singlet state of the monoanion (by 1.199 eV at the SCF/aug-cc-pVDZ level) but electronically unstable with respect to the open-shell states of the monoanion. That is, we end up with the following energy ordering:  $E_{\text{triplet anion}} < E_{\text{open-shell singlet anion}} < E_{\text{dianion}} < E_{\text{closed-shell anion}}$ , which suggests that this dianion could not be formed because it would spontaneously lose one electron (from its Li-CC terminus) to produce the open-shell monoanion.

Clearly, the problem with LiCN··LiCN··LiCC is that the dipole-binding site is stronger than the LiCC valence-binding site. We can correct this deficiency in either of two ways: (i) by decreasing the dipole moment and, as a consequence, the binding energy of the dipole site, or (ii) by increasing the binding strength of the valence site. We decided to explore the latter option because valence binding is a widely studied area and offers a wide range of strengths.

### 5. Adding a stronger valence binding site

Knowing that the electron affinities of the so-called superhalogens are extremely large,<sup>28</sup> we decided to link the -PF<sub>5</sub> functional group to the terminal carbon atom of the LiCN··LiCN··LiCC species discussed above both to lengthen the molecule (and thus reduce  $1/r$ ) and to increase the strength of the valence binding site. With this modification, the ground state of the (LiCN··LiCN··LiCC-PF<sub>5</sub>)<sup>-</sup> monoanion was the closed-shell singlet state with the first extra electron added to its valence binding site (at least at MP2 level of theory, while at the SCF level the open-shell triplet was the ground state of this monoanion). The orbital energy of the lowest unoccupied molecular orbital (LUMO) of this closed-shell monoanion (-0.6 eV) suggested that the

TABLE I. Electron binding energies  $E$  (in eV) for (LiCN··LiCN··LiCC-PF<sub>5</sub>)<sup>2-</sup> with respect to the singlet monoanion at the equilibrium geometry of the dianion and the open-shell triplet and closed-shell singlet states of the monoanion.<sup>a</sup>

$E$	Geometry of <sup>2</sup> A <sub>1</sub> dianion	Geometry of <sup>1</sup> A <sub>1</sub> monoanion	Geometry of <sup>3</sup> A <sub>1</sub> monoanion
$E^{\text{KT}}$	0.764	0.658	0.814
$E^{\text{SCF}}$	0.855	0.747	0.906
$E^{\text{MP2}}$	0.808	0.708	0.855

<sup>a</sup>All results obtained with the aug-cc-pVDZ, basis set augmented with the 4s4p diffuse set centered on the terminal Li atom.

dianion should be stable with respect to the (ground) singlet state. Indeed, our *ab initio* calculations on the dianion show it to be lower in energy (at its equilibrium geometry) than the closed-shell singlet and open-shell triplet states of the corresponding monoanion by 0.808 and 2.546 eV (N.B., the dianion is electronically stable at the equilibrium geometries of both states of the monoanion, see Table I). With this initial success in hand, we subsequently focused our attention on species constructed from LiCN and Li-CC-PF<sub>5</sub>.

## B. The two final candidates

### 1. LiCN··LiCC-PF<sub>5</sub>

Initially, we decided to study the shorter analog of the species just discussed, LiCN··LiCC-PF<sub>5</sub>, which we estimated should be on the border of electronic stability (see below). We anticipated that the reduced dipole moment (compared to the LiCN··LiCN··LiCC system mentioned above) might allow the ground state of the monoanion to be the closed-shell singlet (with the extra electron bound to the valence site) rather than the open-shell triplet (with the extra electron bound to the Li end and a hole at the valence end) even at the SCF level.

By replacing the P atom in LiCN··LiCC-PF<sub>5</sub> by S, we first constructed a neutral closed-shell system LiCN··LiCC-SF<sub>5</sub> whose dipole binding strength we used to estimate that of the parent P-containing radical. The KT estimate of the dipole-binding thus obtained was 1.35 eV. The distance  $r$  between the terminal Li and P atoms of the parent compound was estimated to be 10 Å, which produces a  $1/r$  Coulomb repulsion of 1.4 eV. Therefore, we anticipated that LiCN··LiCC-PF<sub>5</sub> would have a chance of forming a stable dianion, but would likely be marginally stable.

Indeed, we found that the ground state of the singly charged (LiCN··LiCC-PF<sub>5</sub>)<sup>-</sup> species is the closed-shell singlet state (the open-shell triplet state is higher in energy by 0.147 and 1.801 eV at the SCF and MP2 levels, respectively). The second electron binding energy calculated at the KT level and at the equilibrium geometry of the dianion is 0.045 eV (see Table II). Orbital relaxation (given as the difference between the KT and SCF treatments) leads to a significant increase in the electron binding energy (by 0.082 eV). However, the MP2-level correlation correction decreases the binding energy to 0.092 eV. This destabilizing effect is most probably a result of overestimating the dipole moment at the SCF level, and, as a consequence, overestimating the electronic stability of the dianion at this level.

TABLE II. Electron binding energies  $E$  (in eV) for  $(\text{LiCN}\cdots\text{LiCC-PF}_5)^{2-}$  with respect to the singlet monoanion at the equilibrium geometry of the dianion and the monoanion.<sup>a</sup>

$E$	Geometry of ${}^2A_1$ dianion	Geometry of ${}^1A_1$ monoanion
$E^{\text{KT}}$	0.045	-0.060
$E^{\text{SCF}}$	0.127	0.019
$E^{\text{MP2}}$	0.092	-0.009
$E^{\text{MP3}}$	0.122	0.020
$E^{\text{MP4(DQ)}}$	0.121	0.019
$E^{\text{MP4(SDQ)}}$	0.120	0.018
$E^{\text{CCSD}}$	0.120	0.018

<sup>a</sup>All results obtained with the aug-cc-pVDZ basis set augmented with the  $4s4p$  diffuse set centered on the terminal Li atom.

Higher level calculations (see Table II) led to the final value of the electronic stability of this dianion being 0.120 eV at the CCSD level.

Even though the equilibrium geometry of the monoanion does not differ significantly from that found for the dianion (see Table III), the dianion is not stable relative to the monoanion at the equilibrium geometry of the monoanion at the KT level of theory. At this same geometry (i.e., that of the monoanion), the dianion is stable at the SCF level, but the MP2 correlation correction (which is destabilizing) again renders the dianion unstable. Higher level correlation correction is thus necessary to achieve the final answer on the electronic stability of the dianion at this geometry. Such calculations show that the dianion is stable at the MP3, MP4(DQ), MP4(SDQ), and CCSD levels, and the electronic stabilities calculated by these methods seem to converge to our final estimate of 0.018 eV (see Table II).

To fully characterize the nature of the charge distribution in this dianion, we show both the (degenerate) orbital occupied by the valence-bound excess electron and the orbital occupied by the dipole-bound electron in Fig. 2. As can be seen in Fig. 2, the latter electron is mainly distributed outside the molecule but the contributions from the atomic orbitals centered on the Li atom are not negligible.

In summary, the KT,  $\Delta$ SCF and MP2 data presented here do not allow us to conclude with confidence that  $(\text{LiCN}\cdots\text{LiCC-PF}_5)^{2-}$  is actually stable; higher order correlation corrections had to be taken into account to achieve a final answer. Based on our coupled-cluster results, we feel

TABLE III. Geometrical parameters for  $(\text{LiCN}\cdots\text{LiCC-PF}_5)^{n-}$  ( $n=1-2$ ) (bond lengths in Å and valence angle in deg).

Parameter	Monoanion, ${}^1A_1$	Dianion, ${}^2A_1$
$a_1$	1.644	1.653
$b_1$	1.640	1.642
$c_1$	1.816	1.812
$d_1$	1.221	1.222
$e_1$	1.931	1.975
$f_1$	2.007	1.983
$g_1$	1.146	1.150
$h_1$	1.962	2.080
$\alpha_1$	87.888	87.427

reasonably confident in concluding that this dianion is electronically stable and should be detectable experimentally.

Finally, we considered the stability of the  $(\text{LiCN}\cdots\text{LiCC-PF}_5)^{2-}$  dianion with respect to fragmentation and found it to be stable thermodynamically by 3.9 kcal/mol (including ZPE) with respect to  $\text{LiCN}\cdots\text{LiCC}^-$  and  $\text{LiCN}^-$ . According to our findings, there is no kinetic barrier for the rejection of the  $\text{LiCN}^-$  dipole-bound monoanion and the  $\text{LiCN}\cdots\text{LiCC}^-$  monoanion. Since the loss of  $\text{LiCN}^-$  seems to be the most probable (i.e., lowest-energy) fragmentation channel, we conclude that the  $(\text{LiCN}\cdots\text{LiCC-PF}_5)^{2-}$  dianion is a thermodynamically stable species.

## 2. $\text{LiCN}\cdots\text{LiCN}\cdots\text{LiCC-PF}_5$

The dianion of  $\text{LiCN}\cdots\text{LiCC-PF}_5$  is rather weakly bound (electronically and geometrically) according to our findings. Hence, we decided to add another LiCN unit to obtain a larger dipole moment and stronger dipole-binding. The dipole moment of the neutral  $\text{LiCN}\cdots\text{LiCN}\cdots\text{LiCC-PF}_5$  molecule (estimated by replacing the P atom with S) is so large (36.5 D) that the open-shell triplet state again becomes the ground state of the monoanion at the uncorrelated (SCF) level of theory. This state has two unpaired electrons - one localized near the carbon atom connected to the phosphorus and the second localized near the terminal Li atom. However, when electron correlation effects are included, we observe the significant lowering of the total energies of the closed-shell singlet state of the monoanion and the doublet state of dianion, while the decrease of the total energy of the open-shell triplet state of the monoanion is not so large. This is not surprising because it is well known that correlation effects are particularly important for electrons occupying the same molecular orbital. As a consequence, the ground closed-shell singlet state of the monoanion is lower in energy than the triplet state by 1.738 eV at the correlated (MP2) level.

Addition of the second extra electron leads to a doublet dianion that is electronically the most stable species by 0.808 eV relative to the closed-shell singlet monoanion at the MP2 level. To verify that the lowest doublet state is really the ground state of the dianion, we also performed calculations for the lowest quartet state. According to our findings, the lowest quartet state possessing a  $(e)^3(a_1)^1(a_1)^1$  configuration is higher in energy than the doublet state by 2.356 eV at the MP2 level.

The charge distribution of the two excess charges in the dianion is similar to that obtained for more weakly bound  $(\text{LiCN}\cdots\text{LiCC-PF}_5)^{2-}$  species (see Fig. 2).

The geometrical parameters of the singlet and triplet states of the monoanion and the doublet state of the dianion are collected in Table IV. The differences between the corresponding parameters are larger than in the case of the  $(\text{LiCN}\cdots\text{LiCC-PF}_5)^{n-}$  ( $n=1-2$ ) species. The largest change is the contraction of the terminal C-Li bond (parameter  $k_2$ ) by 0.125 Å after the detachment of the second extra electron to form the ground, closed-shell singlet monoanion. If one compares the geometries of the dianion and (excited) triplet state of the monoanion, a significant elongation is

TABLE IV. Geometrical parameters for  $(\text{LiCN}\cdots\text{LiCN}\cdots\text{LiCC-PF}_5)^{n-}$  ( $n=1-2$ ) (bond lengths in Å and valence angle in deg).

Parameter	$^1A_1$ Monoanion	$^3A_1$ Monoanion	$^2A_1$ Dianion
$a_2$	1.647	1.608	1.651
$b_2$	1.640	1.621	1.641
$c_2$	1.815	1.868	1.813
$d_2$	1.222	1.224	1.222
$e_2$	1.946	2.268	1.967
$f_2$	1.989	1.855	1.986
$g_2$	1.148	1.151	1.149
$h_2$	2.006	2.089	2.049
$i_2$	1.948	1.875	1.909
$j_2$	1.146	1.152	1.151
$k_2$	1.986	2.130	2.111
$\alpha_2$	87.739	90.722	87.517

found (by 0.301 Å) in the C–Li bond in the CC–Li fragment when the excess electron is detached and the triplet state is formed. This is caused by the fact that one of the unpaired electrons in the triplet state is localized in this region of the molecule (see Fig. 2).

As far as the stability of  $(\text{LiCN}\cdots\text{LiCN}\cdots\text{LiCC-PF}_5)^{2-}$  dianion with respect to fragmentation is concerned, we found the thermodynamic barrier for the most probable fragmentation channel (i.e., the loss of  $\text{LiCN}^-$ ) to be 36.5 kcal/mol (including ZPE). Similarly to the previously described dianion  $[(\text{LiCN}\cdots\text{LiCC-PF}_5)^{2-}]$ , there is no kinetic barrier for the rejection of the  $\text{LiCN}^-$  dipole-bound monoanion. Thus we conclude that the  $(\text{LiCN}\cdots\text{LiCC-PF}_5)^{2-}$  dianion is a thermodynamically stable species.

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