

A dipole-bound dianion

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The possibility of binding two electrons by the dipole potential of a molecule was examined earlier by us using model potentials. That study suggested that large dipole moments $\mu = qR$ and large charge separation distances R (or equivalently large charges q) would be required to achieve binding two electrons. For example, even with a charge $q = 1.5$ a.u. which might be achieved using di- or tri-valent cations, a dipole moment exceeding 15.922 D is needed. The presence of inner-shell electrons even further increases the value of μ that is required because the dipole-bound electrons' orbital must be orthogonal to and excluded from such inner shells. In the present work, we discuss our efforts to find a real molecule that can actually bind two electrons to a single dipole site. Numerical results are presented for the mono- and dianions of a double 5-member carbon ring system substituted with a Ca atom and three superhalogen $-\text{PF}_5$ groups. The dianion of this molecule is found to be geometrically stable and to have a vertical electron detachment energy of ca. 0.8 eV. Its two excess electrons occupy the same fully symmetric a_1 molecular orbital localized at the electropositive Ca end of the neutral system as is routinely observed in dipole-bound monoanions. Although our final candidate is chemically unusual, it is hoped that our predictions about it will encourage others to search for more synthetically tractable alternatives. © 2000 American Institute of Physics. [S0021-9606(00)30915-1]

I. INTRODUCTION

A. Monoanions

It is well known that dipole-bound singly charged anions can be electronically stable if the dipole moment μ of the neutral molecular host exceeds 1.625 D.¹ In particular, for dipole moments greater than this critical value, there are an infinity of bound states within the context of the Born–Oppenheimer (BO) approximation (i.e., when the dipole is not vibrating or rotating). It has also been shown that the same critical dipole moment that applies to the point dipole potential (for which the potential $V = -\mu e \cos \theta / r^2$) also applies to fixed nonrotating finite dipoles, even if a short-range repulsive core potential is present.^{2–4} Moreover, Jordan and Luken showed that (i) the loosely bound electron in a dipole-bound state occupies a diffuse orbital localized mainly on the positive side of the dipole,⁵ and (ii) the repulsion and exclusion effects due to inner shell electrons increase the critical dipole moment to at least 2D to achieve a binding energy of ca. 1 cm^{-1} .

Depending on the electron binding energy, the average distance between the extra electron and the positive center of the dipole can be quite large (10–100 Å).⁶ Garrett studied the role of non-BO coupling and concluded that such couplings are negligible for dipole-bound states with electron binding energies (E) much larger than molecular rotational constants.⁷ Finally, it was recently demonstrated for a num-

ber of systems^{8–13} that electron correlation effects play important roles in determining the binding energies even though the weakly bound electron resides far from the molecular framework in a diffuse orbital.

For all of these reasons, the study of dipole-bound anions has proven to be a challenge to theoreticians and has become an area of more and more experimental effort and interest.

B. Dianions

As far as multiply charged molecular anions are concerned, the experimental and computational studies have primarily been limited thus far to valence-bound species.^{14–18} In addition, we recently studied the possibility of binding two electrons to a molecule utilizing two distinct electron binding sites, one valence- and one dipole-binding center.¹⁹ We 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 site, the dianion can be electronically stable with respect to the corresponding monoanion. Moreover, for reasonable valence- and dipole-binding strengths, the distance between the two sites can be small enough to be realized in experimentally accessible molecules. We studied two such molecules $[(\text{LiCN})_n \cdots \text{LiCC} \rightarrow \text{PF}_5]$, $n = 1–2$ using *ab initio* electronic structure methods and predicted their dianions' vertical electronic stabilities to be 0.120 and 0.808 eV, for $n = 1$ and 2, respectively. We also found these dianions to be geometri-

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cally and thermodynamically stable systems. This investigation into mixed valence- and dipole-bound anions taught us that one can use so-called *superhalogen*²⁰ groups such as $-\text{PF}_5$ to create a highly localized negative charge center in the molecule (i.e., the superhalogens prevent the negative charge from being distributed throughout the molecule) which binds its electron tightly enough to overcome Coulomb repulsion from another nearby anion site.

We also recently studied the possibility of binding two electrons to a model fixed finite dipole potential²¹ consisting of two charges $+/-q$ separated by a distance R . We found that the critical value of the dipole moment $\mu = qR$ required to bind two electrons strongly depends on q . This is unlike the case when one electron is bound to the same potential for which the critical binding depends only on the product qR . Moreover, we showed computationally that the critical value of the dipole moment required to bind two electrons by ca. 1 cm^{-1} approaches a value below 2D in the "point-dipole" limit of large q and small R . In addition, we showed analytically (based on the analysis of the q -dependence of the two-electron fixed-finite-dipole Hamiltonian) that, in the point-dipole limit, the critical dipole value for infinitesimal binding indeed approaches that for binding a single electron (1.625 D).

More recently, Sarasola *et al.* also computationally studied, within the fixed finite dipole model, the critical conditions for stable dipole-bound dianions. In their study, only the cases for $q = 1, 2,$ and 3 were examined and neither our finding of strong dependence of the critical dipole moment on q nor our conclusion that the critical dipole moment for two electrons approaches 1.625 D in the point-dipole limit, were noted.²²

Based on our experience on dipole-bound monoanions, mixed valence/dipole-bound dianions, as well as our model studies on binding two electrons to the fixed finite dipole potential, we decided to undertake efforts to design a real (perhaps experimentally accessible) molecule that matches our formulated requirements²¹ for binding two excess electrons by its dipole potential. In this work, we report our numerical results for such a molecule. The species that we ultimately (after much trial and error as detailed in Sec. III A) propose is constructed from two 5-member carbon rings substituted with an electropositive Ca atom and three superhalogen $-\text{PF}_5$ groups (denoted compound **1** in the text and in Fig. 1), which, according to our findings, can bind two electrons by its dipole potential. Our findings on this species as well as on other molecules that we tested are detailed in Sec. III.

II. METHODS

The equilibrium geometries of the neutral and anionic species derived from **1** have been optimized and their harmonic vibrational frequencies calculated at the second-order Møller–Plesset (MP2) perturbation theory²³ level. In all calculations, the values of $\langle S^2 \rangle$ never exceeded 2.0750 for triplets, and 0.7510 and 3.7505 for doublet and quartet states, respectively so we are confident that spin-contamination effects are not serious. The electronic stabilities of the anions in their ground states were calculated using a supermolecular

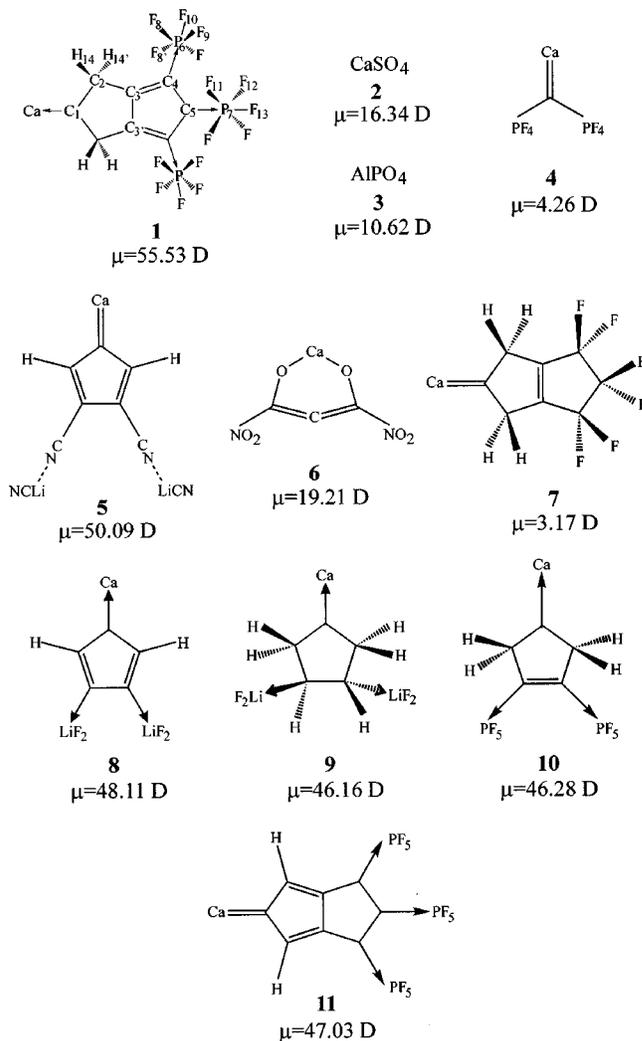


FIG. 1. Schematic structures of various compounds discussed in this work and corresponding values of their dipole moments.

approach (i.e., by subtracting the energies of the anion from those of the neutral). In addition, the electron-binding energies were analyzed within the perturbation framework described in Ref. 10, which generates Koopmans' theorem (KT),²⁴ self-consistent-field (SCF) difference (ΔSCF), and Møller–Plesset difference (MP2) values of the binding energies. Since the system studied contains 27 heavy atoms (which led to almost 500 contracted basis functions), we had to limit the level of our calculations to the MP2 level.

All calculations were performed with the GAUSSIAN 98 program,²⁵ on 500 MHz dual processor Intel Pentium III computers and on an SGI Origin2000 numerical server. The three-dimensional plots of molecular orbitals were generated with the MOLDEEN program.²⁶

The choice of the atomic orbital basis sets used to describe the neutral molecule and the excess bound electrons is very important for reproducing the correct value of the electron-binding energy. The basis sets must be flexible enough to describe the static charge distribution of the neutral molecular host, and to allow for polarization and dispersion stabilization of the anions upon electron attachment. For these purposes, we used the 6-31G(d,p) basis set²⁷ since an

aug-cc-pVDZ basis set²⁸ (which has proved to be very reliable for studying many dipole-bound anions) is not currently available for calcium. For consistency, we employed the 6-31G(d,p) bases for C, F, P, and the 6-31G(p) basis for H. We supplemented the Ca 6-31G(d,p) basis set with diffuse functions having very low exponents, which was necessary especially in order to describe properly the dianion's pair of excess electrons. In particular, we supplemented the 6-31G(d,p) basis set with extra even-tempered²⁹ five-term s and five-term p sets of diffuse functions centered on the Ca atom. The extra diffuse s and p functions share exponent values and the geometric progression ratio was equal to 3.2,³⁰ and we started to build up the exponents from the lowest sp exponent included in the 6-31G(d,p) basis set designed for calcium. As a consequence, we achieved lowest exponents of 7.751584×10^{-5} a.u. for both s and p symmetries.

We verified that the MP2 electron-binding energy of the dianion increases by less than 0.01 eV if one more set of s and p diffuse functions is added to the Ca basis. In addition, we replaced the 6-31G(d,p) bases on all atoms with the Schäfer, Horn, and Ahlrich double-zeta basis set,³¹ keeping our five-term Ca sp diffuse set fixed. This replacement increased the MP2 electron-binding energy of the dianion by less than 0.1 eV.

The atomic partial charges calculated in this work were fitted to the electrostatic potential according to the Merz–Singh–Kollman scheme.³² Moreover, these charges, as well as the dipole moment of the neutral molecule, were examined for convergence as yet another test of our basis quality, as the diffuse part of our basis set was altered. We found good convergence of the charges and dipole moment as 3, 4, and then 5 diffuse basis sets were added and that addition of a sixth set of diffuse functions to the basis changes the atomic partial charge on Ca and the total dipole moment by less than 0.000 05 a.u. and 0.0005 D, respectively.

III. RESULTS

Our search for a dipole-bound dianion (detailed further below) eventually led us to a species constructed from two 5-member carbon rings substituted with a Ca atom and three superhalogen $-PF_5$ groups, called compound **1** (see Figs. 1 and 2) which we determined can indeed form such a state and for which we present detailed findings below in Sec. III B. For this molecule, the two excess electrons are dipole-bound and occupy the same molecular orbital that Fig. 3 shows is localized on the positive Ca end of the molecular dipole.

Before describing our results in detail, we discuss the search that culminated in this candidate for binding two electrons by the dipole potential because we believe useful information was learned in this search.

A. Strategy for designing a dipole-bound dianion that produced compound **1**

As in every dipole-bound monoanion, the neutral (parent) molecule possesses certain properties, among which the most important are (i) its ground electronic state should be a closed-shell singlet state so that no empty or half-filled va-

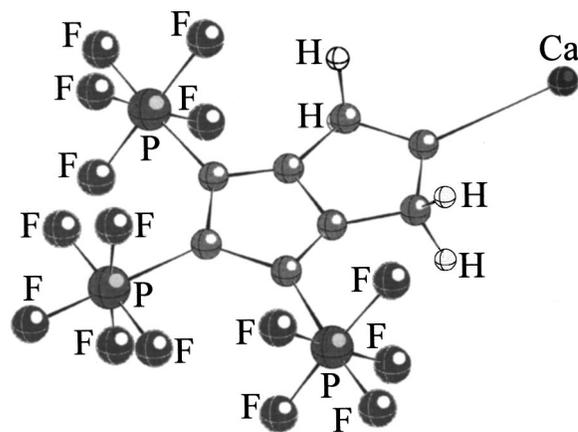


FIG. 2. The MP2 equilibrium C_{2v} geometry of the ground electronic closed-shell singlet state of the dianion of compound **1**.

lence orbitals exist, and (ii) the dipole moment should be large enough to bind an excess electron. In addition, in the case of dipole-bound *dianions*, the charge q from which the molecular dipole is constructed must be large enough to satisfy the critical binding conditions (described previously²¹). Recall that, unlike dipole-bound monoanions, the critical value of the dipole moment required to bind *two* extra electrons strongly depends on the charge q , not only on the dipole qR .

Of course, there are expected to be difficulties in adopting our model dianion results²¹ to predict the behavior of real chemical systems. First, although the dipole moment is a well-defined quantity, the partial charge q (or alternatively, the charge separation R) is not. Our computed partial atomic charges depend on the kind of population analysis used. Moreover, the exclusion and orthogonality effects of inner-shell orbitals should be also taken into account as noted in our earlier study.²¹ These latter restrictions produce even larger critical values of q and μ (to achieve two-electron binding) than those predicted by the fixed finite dipole model.

Keeping all these limitations and pessimistic predictions (i.e., the need for exceptionally large μ and q) in mind, we decided to design several neutral molecules having dipole moments much greater than necessary according to the model results of Ref. 21. We decided to use a divalent alkaline-earth metal atom (Ca) as the positive center of the

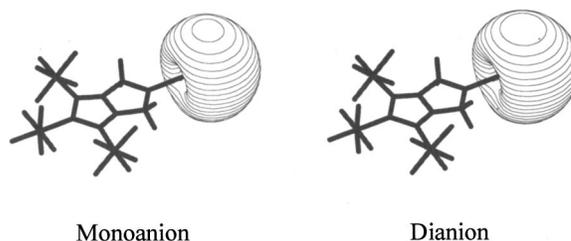


FIG. 3. Singly occupied a_1 molecular orbital for the 2A_1 ground electronic state of the monoanion of **1** (left) and highest doubly occupied a_1 molecular orbital for the 1A_1 ground electronic state of the dianion of compound **1** (right).

molecular dipole because we knew²⁰ that the partial charge $+q$ had to be >1 to achieve binding with any achieved dipole.

Before discussing further our findings, let us briefly elaborate on the series of molecules examined that finally led us to molecule **1** so the reader can better understand the need for the unusual structure we eventually proposed. In every case described further (systems **2-11**, Fig. 1), we performed geometry optimization of the neutral molecule at the SCF/6-31+G(d,p) level and we calculated the dipole moment and the atomic partial charges (we use those fit to the electrostatic charge density according to the Merz–Singh–Kollman scheme) from the SCF density using the same basis set. If the initial results were promising, as judged by the magnitudes of the dipole and charge q^{Ca} , we calculated the electronic stabilities of the corresponding mono- and dianion at the SCF and MP2 level to check whether the dianion might be an electronically stable species.

According to our critical conditions formulated elsewhere,²¹ the neutral molecule must possess a very large dipole moment and have positive charge significantly larger than 1.0 on its electropositive end. Therefore, we focused our search on molecules having di- and tri-valent metal atoms as the electropositive center. We started with the well-known ionic compounds **2** and **3** (see Fig. 1) for which we expected substantial atomic charge localized on the Ca and Al, respectively. Indeed, the calculated charges were large ($q^{\text{Ca}} = 1.53$ a.u., $q^{\text{Al}} = 1.06$ a.u.), but the nearest negatively charged ($q^{\text{O}} = -1.10$ and -0.77 a.u. for **2** and **3**, respectively) oxygen atoms were too close to the positive center, which caused the dipole moment to be too small (16.34 and 10.62 D for **2** and **3**, respectively) to bind two excess electrons. System **4** was even worse because the atomic partial charge localized on the Ca atom was close to zero and the dipole moment was small (4.26 D). Species **4** involves a double (σ and π) bond between Ca and the neighboring carbon, as well as two electronegative $-\text{PF}_4$ groups. Note that $-\text{PF}_4$ groups are *not* superhalogens whereas $-\text{PF}_5$ is a superhalogen.

Next, we decided to use extended carbon rings to construct our molecule to obtain larger separation of the polar ends. We also used LiCN molecules to increase the dipole moment of system **5** since these groups are known to be very polar.¹⁹ The resulting dipole moment was very large (50.09 D), however, the charge on Ca $q^{\text{Ca}} = 0.94$ a.u. was too small to bind two extra electrons. Even if the dianion of **5** were stable electronically, it would most likely be unstable thermodynamically with respect to the loss of two LiCN monoanions.

Next, by including the Ca atom in a ring and using $-\text{NO}_2$ groups to increase the polarity of the system we constructed (**6**) ($\mu = 19.21$ D, $q^{\text{Ca}} = 1.59$ a.u.), but again we were unable to bind two electrons. Then, we tried to use halogen atoms separated from the positive end of the molecule by two 5-member carbon rings (**7**) but, surprisingly, we obtained a very small dipole moment (3.17 D). Finally, we decided to use more drastic means and we started to design our candidates utilizing superhalogen groups that are known to possess extremely large electron affinities.²⁰

In the beginning, we tried one of the smallest superhalogens (LiF_2) to construct candidates (compounds **8** and **9**) and we obtained very promising preliminary results. The dipole moments were equal to 48.11 and 46.16 D for **8** and **9**, respectively, and the partial charges for Ca were satisfactory (1.66 and 1.61 a.u. for **8** and **9**, respectively). However, these two species were not geometrically stable but underwent fragmentation to eliminate LiF and HF molecules. Nevertheless, their strong electron binding strengths helped us take the next step in our design process.

We constructed **10** from stronger superhalogen groups ($-\text{PF}_5$) connected to the carbon ring through dative rather than covalent bonds. Our detailed analysis of all occupied molecular orbitals in **10** led us to the conclusion that the Ca atom is also connected to the ring by a dative bond, as a result of which there is the only one π -bond in that system (localized as indicated in Fig. 1). The partial atomic charge on Ca calculated for **10** was as large as 1.53 a.u. and the dipole moment was found to be 46.28 D. Although we were optimistic, we found the dianion to be electronically *unstable* both at the SCF and MP2 levels. There can, of course, be many reasons why this species that fulfills the formulated requirements cannot bind two excess electrons. We think the most likely is the crude estimate of the charge q in the molecule since the model suggests the critical dipole moment strongly depends on q . Also, the presence of inner shell electrons will act to destabilize the dianion as in dipole-bound monoanions.

Hence we decided to add another $-\text{PF}_5$ group to the molecule and to increase the separation between the Ca atom and $-\text{PF}_5$ groups to obtain a larger dipole moment. The resulting compound (**11**) did not possess a significantly larger dipole moment than **10** and had $q^{\text{Ca}} = 1.51$ a.u. Careful analysis of its electronic structure indicated that the Ca atom is connected to the carbon ring by a double bond in which the nearest C atom is negatively charged ($q^{\text{C}} = -0.44$ a.u.), which therefore decreases the polarity of the system. Moreover, we checked that two C–C π bonds were present in this molecule and localized in the ring which is closer to the Ca atom. This kind of charge distribution caused a substantial decrease of the dipole moment value, and we found the dianion of **11** to be electronically stable at the neither SCF nor MP2 level.

However, our studies on the properties of **10** and **11** suggested how we could alter **11**'s charge distribution to produce a structure with a significantly larger dipole moment and a large q^{Ca} . One way to change this charge distribution was to make the Ca–C bond a two-electron dative bond rather than the covalent two-electron σ and two-electron π bonds as in **11**. Thus, we added two more H atoms to the carbon ring closest to Ca, making it a more saturated part of the molecule. As a consequence, we obtained a structure possessing a C→Ca dative bond and two π bonds localized in the second carbon ring (see compound **1** in Fig. 1) with a dipole moment $\mu = 55.53$ D and $q^{\text{Ca}} = 1.73$ a.u. The two electrons in **11** are involved in the Ca–C π bond shift to the C→P dative bonds of C_4 (and its equivalent C) in **1**. We found the dianion of compound **1** (for which the detailed results are in Sec. III B) electronically stable with respect to

TABLE I. The MP2 equilibrium geometries for the neutral 1A_1 , monoanion 2A_1 , and dianion 1A_1 ground electronic states at the C_{2v} minima^a [distances (r) in Å, valence (α), and dihedral (γ) angles in degrees].

Parameter	Neutral molecule	Monoanion	Dianion
$r(C_1C_2)$	1.482	1.489	1.495
$r(C_2C_3)$	1.492	1.495	1.498
$r(C_3C_4)$	1.316	1.320	1.324
$r(C_4C_5)$	1.549	1.542	1.535
$r(C_3C_3')$	1.472	1.479	1.486
$r(C_1Ca)$	2.512	2.632	2.820
$r(C_2H_{14})$	1.093	1.090	1.089
$r(C_4P_6)$	1.907	1.903	1.899
$r(C_3P_7)$	1.947	1.947	1.948
$r(P_6F_8)$	1.654	1.647	1.640
$r(P_6F_9)$	1.584	1.591	1.596
$r(P_6F_{10})$	1.599	1.608	1.616
$r(P_7F_{11})$	1.609	1.610	1.612
$r(P_7F_{12})$	1.581	1.580	1.580
$r(P_7F_{13})$	1.581	1.592	1.602
$\alpha(CaC_1C_2)$	124.77	125.38	125.86
$\alpha(C_1C_2C_3)$	106.84	106.93	107.70
$\alpha(C_2C_3C_3')$	108.86	108.49	108.19
$\alpha(H_{14}O_2H_{14'})$	103.31	103.53	103.64
$\alpha(H_{14}C_2C_3)$	112.82	112.67	112.62
$\alpha(C_3'C_3C_4)$	113.32	112.90	112.48
$\alpha(C_3C_4C_5)$	102.44	102.76	103.05
$\alpha(P_6C_4C_5)$	140.13	139.50	138.90
$\alpha(F_8P_6F_8')$	86.51	87.14	87.70
$\alpha(F_8P_6F_{10})$	88.33	88.25	88.18
$\alpha(F_9P_6F_{10})$	90.94	90.19	89.51
$\alpha(F_8P_6F_9)$	89.34	89.25	89.15
$\alpha(F_{10}P_6C_4)$	174.05	174.76	175.42
$\alpha(F_{11}P_7F_{12})$	89.98	90.04	90.07
$\alpha(F_{11}P_7F_{13})$	94.98	94.28	93.64
$\gamma(H_{14}C_2H_{14'}C_3)$	122.13	122.01	122.00

^aFor the atom numbering, see Fig. 1.

the corresponding monoanion, so we finished our search and we focused on determining the properties of that system.

B. The final candidate

1. The neutral system

Let us begin by describing the electronic structure of the neutral parent (Fig. 1) which is not trivial. This compound possesses a minimum at C_{2v} symmetry, where its ground electronic state is a closed-shell singlet 1A_1 . The lowest triplet state is higher in energy by 3.467 eV (at the MP2 level). One can imagine at least a few different structural formulas for this compound, corresponding to various resonance structures. The unusual structural picture proposed by us was made only after a detailed analysis of all molecular orbitals (MO) containing the valence electrons, as well as of the population analysis and the interatomic distances. We are, after examining the nature of the occupied orbitals, confident that there are two well-localized double bonds and the four dative bonds discussed earlier. Our structural formula is shown in Fig. 1 (compound **1**), while the details of the equilibrium geometry are given in Table I.

Compound **1** consists of two 5-member rings that share two carbon atoms. Three $-PF_5$ superhalogen groups (which are *not* simply PF_5 molecules, but have a nearly octahedrally coordinate P atom surrounded by five F atoms plus a vacant

orbital) are connected to the molecule by dative bonds to the neighboring C atoms, as indicated in Fig. 1. The $-PF_5$ group can be considered as created by removing an F^- anion from the well-known octahedral superhalogen PF_6^- . Since PF_6^- is a closed-shell anion, the neutral $-PF_6$ is also closed-shell; however, it possesses an empty orbital that acts as an electron pair acceptor. Our analysis of the LCAO coefficients confirms this speculation. A similar situation is observed in the case of the Ca atom connected to the C atom in the other ring. As noted earlier, the two valence electrons of the Ca have moved to C_4 and its equivalent C to help form $C \rightarrow P$ bonds, so Ca becomes positively charged which opens the possibility of it participating as an acceptor in a dative bond to its neighbor C.

The existence of four dative bonds in which carbon atoms act as donors, and the presence of four H atoms connected to two other carbons, limits the number of possible resonance structures that can be drawn for compound **1**. We carefully analyzed the full set of valence MO orbitals and concluded that there are only two π bonds in the system, as we indicated in Fig. 1. The analysis of the bond lengths confirms this proposition. Indeed, these two double bonds are the shortest carbon-carbon bonds with an equilibrium distance (1.316 Å) similar to the typical $C=C$ bond existing in organic compounds. By contrast, all other carbon-carbon bonds are in the 1.47–1.55 Å range and correspond rather to typical single C-C bonds (see Table I and Figs. 1 and 2).

Molecule **1** is extremely polar with a Ca partial atomic charge (fitted to the electrostatic potential according to the Merz-Singh-Kollman scheme) of +1.682 a.u., and a dipole moment of 55.53 D. Its lowest unoccupied molecular orbital (LUMO) is localized on the positive side of the molecule near the Ca atom. According to our previous findings, such a neutral system should be able to bind two excess electrons by its dipole potential.

2. The dipole-bound monoanion

The neutral molecule **1** in its ground 1A_1 electronic state possesses 12 virtual orbitals having negative eigenvalues. This indicates that not only the ground state of the monoanion but also many excited states might be (vertically) electronically bound with respect to the ground state of the neutral molecule. Even though this finding is interesting, since bound-excited anionic states are rather unusual, we will not pursue these excited states in this effort. Rather, we focus on the ground electronic state of the monoanion of **1**, which we found to be a 2A_1 state. We also verified that the energy of the lowest quartet state of the monoanion is higher than for the lowest doublet 2A_1 state by 0.517 eV at the MP2 level.

The monoanion of **1** possesses a minimum at C_{2v} symmetry with the geometrical parameters given in Table I. The open-shell doublet A_1 state of the monoanion is strongly bound because of the extremely large dipole moment of its neutral parent. Its singly occupied molecular orbital (SOMO) is depicted in Fig. 3, and, as in other well-known dipole-bound monoanions, is localized on the electropositive site of the molecular dipole (near the Ca atom).

The vertical electron binding energies corresponding to the attachment of the first excess electron are gathered in

TABLE II. Vertical first electron binding energies E (in eV) for the ground 2A_1 electronic state of the compound **1** monoanion at the equilibrium C_{2v} geometries of the neutral, monoanion, and dianion.^a

E	Geometry of 1A_1 neutral	Geometry of 2A_1 monoanion	Geometry of 1A_1 dianion
E^{KT}	5.425	5.612	5.834
E^{SCF}	5.669	5.857	6.086
E^{MP2}	2.142	2.316	2.515

^aAll results obtained with the 6-31G(d,p) basis set augmented with the 5(*sp*) diffuse set centered on the Ca atom.

Table II for various theoretical methods. We calculated these energies for the equilibrium geometry of the neutral **1** as well as those of its mono- and dianion. The same trend can be observed for each geometry—a very large electron binding energy calculated at the KT level (5.4–5.8 eV) is close to the corresponding SCF binding energy (5.7–6.1 eV), and the orbital relaxation, in all cases, acts to stabilize the monoanion. Moreover, at all three geometries we observe dramatic destabilization of the monoanion when electron correlation effects are included (at the MP2 level). The electron binding energy drops by 3.5 eV and the resulting values of E are in the 2.1–2.5 eV range.

This unusual behavior (correlation effects in most dipole-bound monoanions act in the opposite direction, i.e., they *stabilize* the anionic species) puzzled us. We initially thought that the SCF description of the charge distribution for the neutral molecule might be significantly overestimating the dipole moment which could cause overestimation of the electron binding energy for the monoanion. In order to check this postulate, we calculated the dipole moment for the neutral using the MP2 electron density (μ^{MP2}) and compared it to μ^{SCF} derived from the SCF density (see Table III). We found that the anticipated overestimation appeared to be not very large (2.0–2.3 D) and thus is not likely responsible for the large destabilization we observed.

We therefore decided to take a closer look at the electron pair correlation contributions that constitute the second-order correction to the electronic energy (E_2) for both the neutral and anionic system. We denote by $\epsilon(ij)$ the MP2 estimate of the correlation energy for the pair of occupied spin-orbitals labeled i and j . Each such $\epsilon(i,j)$ is expressed in terms of a sum over pairs of virtual orbitals ν, ν' of contributions $\epsilon(i,j|\nu,\nu') = |\langle ij|\nu\nu'\rangle|^2 / (e_i + e_j - e_\nu - e_{\nu'})$. Our detailed analysis of all such pair contributions led us to conclude that

TABLE III. Dipole moments (in D) and Ca partial charges (in a.u.) of the neutral molecule for the equilibrium geometries of the neutral, monoanion, and dianion (calculated from SCF and MP2 densities). The partial charges are fitted to the electrostatic potential according to the Merz–Singh–Kollman scheme.

	Geometry of 1A_1 neutral	Geometry of 2A_1 monoanion	Geometry of 1A_1 dianion
μ^{SCF}	55.526	58.013	60.976
μ^{MP2}	53.572	55.978	58.712
q^{SCF} (Ca)	1.727	1.740	1.753
q^{MP2} (Ca)	1.682	1.694	1.700

the large reduction in the electron binding energy from ΔSCF to the MP2 level results primarily from three groups of terms: $\sum_{\nu\nu'} \epsilon(60,j|\nu,\nu')$, $\sum_{\nu\nu'} \epsilon(61,j|\nu,\nu')$, and $\sum_{\nu\nu'} \epsilon(62,j|\nu,\nu')$, where j runs through all occupied valence spin-orbitals, and orbitals 60, 61, and 62 are constructed primarily from $3p_x$, $3p_y$, and $3p_z$ atomic Ca orbitals, respectively. Further analysis of these particular contributions indicated that the most important among them are $\sum_{\nu\nu'} \epsilon(60,60|\nu,\nu')$, $\sum_{\nu\nu'} \epsilon(61,61|\nu,\nu')$, $\sum_{\nu\nu'} \epsilon(62,62|\nu,\nu')$ (which is not surprising) as well as $\sum_{\nu\nu'} \epsilon(60,53|\nu,\nu')$, $\sum_{\nu\nu'} \epsilon(61,52|\nu,\nu')$, and $\sum_{\nu\nu'} \epsilon(62,j|\nu,\nu')$, where $j=55, 56, 98, 110, 121$. Since the orbitals numbered 52, 53, 55, 56, 98, 110, and 121 are localized primarily on the $-\text{PF}_5$ groups, we can conclude that the significant decrease in electron-binding energy from ΔSCF to MP2 is related to loss of electron correlation energy (moving from the neutral to the anion) inside the neutral molecule, which primarily involves $3p$ Ca electrons correlating with other Ca $3p$ electrons and with electrons on the $-\text{PF}_5$ superhalogen groups.

3. The dipole-bound dianion

An attachment of a second excess electron to molecule **1** leads to the formation of an electronically and geometrically stable doubly charged anionic species which we believe is the first dipole-bound dianion that has been proposed in the literature. Our conclusion about its dipole-bound nature is based on the facts that (i) its neutral parent is a closed-shell singlet molecule with a very large dipole moment (see Sec. III B 1), (ii) the critical conditions formulated by us previously²¹ for dipole-bound dianions are fulfilled, (iii) the two excess electrons occupy the same diffuse fully symmetric a_1 molecular orbital localized on the electropositive site of the molecular dipole (see Fig. 3), and (iv) the geometrical changes after attachment of the first and second extra electron are small and increase both the dipole moment and the atomic partial charge q^{Ca} of the neutral system (see Tables I and III).

The dipole-bound dianion of **1** is a closed-shell system in its ground electronic 1A_1 state. The equilibrium geometry of this dianion (depicted in Fig. 2) possesses C_{2v} symmetry and the bond lengths, as well as valence and dihedral angles are collected in Table I. Compared to the geometries of the monoanion and the neutral molecule (see also Table I), the changes are rather small (as it is usually observed for dipole-bound monoanions). In particular, for all bond lengths (except $\text{C}_1 \rightarrow \text{Ca}$), the differences are less than 0.025 Å, while the changes in angles (valence and dihedral) are usually as small as 1° and never exceed 2°. The only more significant change in geometrical parameters occurs for the $\text{C}_1 \rightarrow \text{Ca}$ dative bond length which increases from 2.512 Å (neutral), to 2.632 Å (monoanion), and then to 2.820 Å (dianion). This important change leads (together with other small geometrical changes) to an increase in the dipole moment of the neutral species as shown in Table III, where these values are reported. Focusing only on the dipole moments derived from the MP2 density, we observe that the geometry changes act to increase the dipole moment by 2.406 D (after attachment of the first electron) and by another 2.734 D (after attach-

TABLE IV. Vertical second electron binding energies E (in eV) for the ground 1A_1 electronic state of compound **1** dianion at the equilibrium C_{2v} geometries of the neutral, anion, and dianion.^a

E	Geometry of 1A_1 neutral	Geometry of 2A_1 monoanion	Geometry of 1A_1 dianion
E^{SCF}	0.090	0.247	0.446
E^{MP2}	0.494	0.651	0.846

^aAll results obtained with the 6-31G(d,p) basis set augmented with the 5(*sp*) diffuse set centered on the Ca atom.

ment of the second electron). One can also notice a similar tendency (in the direction to stabilize the mono- and dianion) by analyzing the Ca atomic partial charges in the neutral molecule calculated for these three geometries (see Table III). As the extra electrons are attached to the neutral system, the atomic partial charges q^{MP2} (and also q^{SCF}) on Ca increase, which also contributes to the increase of the dipole moment.

As far as the highest occupied molecular orbital in the dianion is concerned, we already characterized it as having a_1 symmetry and being localized at the positive side of the molecule (near the Ca atom). Comparison between the singly occupied MO for the monoanion (a_1^1) and the highest doubly occupied MO for the dianion (a_1^2) shows that they have similar shapes and sizes (see Fig. 3) although the latter is, of course, somewhat more diffuse.

Finally, let us discuss the electronic stability of the dipole bound dianion. Since the detailed results can be found in Table IV, we focus on the vertical detachment energies for the second electron (i.e., on the vertical results for the dianionic geometry) because this energy would be most directly related to experimental photodetachment data on this species should such become available. The electron-binding energy calculated at the SCF level was found to be 0.446 eV. This relatively small value suggests that any geometry change that decreases the dipole moment may even cause the dianion to become unstable relative to the monoanion. Indeed, our computed SCF second electron binding energy for the geometry of the neutral shows that, for such a configuration of the nuclei, the dianion would be only barely electronically stable (by 0.090 eV). Even though the electronic stability at the SCF level might be uncertain for some geometries, the inclusion of electron correlation effects (at the MP2 level) leads to significant stabilization of the dianionic species at all geometries. This is caused primarily by the intrapair electron correlation between the two excess electrons that occupy the dipole-bound a_1 molecular orbital. Our final estimation of the vertical detachment energy for the dianion is 0.846 eV, but we realize that higher-order calculations, which we do not presently have the resources to perform, may alter this prediction.

Finally, as a further test of the basis-set dependence of our results, we calculated the vertical detachment energy for the second electron of the dianion at the MP2 level using the Schafer, Horn, and Ahlrich double-zeta basis set³¹ plus our extra 5(*sp*) set of diffuse functions. We found the electron binding energy to be 0.778 eV, which is close to the 0.846

eV obtained with 6-31G(d,p)+5(*sp*) basis set reported in Table IV.

IV. CONCLUSIONS

Our results indicate that binding of two excess electrons by a polar molecule is possible, but the requirements that must be fulfilled by a candidate neutral system are stronger than those described previously²¹ for the fixed finite dipole model.

We propose that the molecular system **1** consisting of two 5-member carbon rings substituted with three superhalogen – PF₅ groups and one Ca atom is capable of binding two extra electrons via its dipole potential. According to our results, the vertical energy for the detachment of the first electron from this dianion should be equal to 0.846 eV.

As noted in the abstract and elsewhere, the electronic structure of our final candidate species **1** is quite unusual primarily because it contains dative bonds and superhalogen groups. We expended considerable efforts to find less unusual molecules that had very large μ and q values but eventually converged on species **1**. Although chemical synthesis of **1** and subsequent detection of its ability to bind two excess electrons may be extremely difficult, it is our hope that the concrete suggestions put forth here will inspire other workers to create more synthetically tractable candidate molecules.

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