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On the existence and characterization of molecular electrideres[†]Verònica Postils,^a Marc Garcia-Borràs,^a Miquel Solà,^a Josep M. Luis,^{a*} and Eduard Matito^{a*}

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Electrideres are ionic compounds thus far occurring in solid state, where the anionic part is constituted by isolated electrons. We herein provide an unambiguous computational means to distinguish electrideres from similar species, proving the existence of some electrideres in gas phase. We also put forward a recipe to design new electrideres.

Electrideres are among the most intriguing species lately discovered. These ionic compounds, postulated and synthesized by J. L. Dye,^{1–4} have electrons occupying the anionic positions of solid compounds. They eluded room temperature stability until the group of Hosono produced $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{68}]4\text{e}^-$, the first stable electrideres.^{5,6} Thereupon, these compounds have found a plethora of applications,^{7–10} ranging from an electron emitter¹¹ to a reversible H_2 storage device.¹² Perhaps the most fascinating realization of an electrideres is the transformation of mayenite, a component of alumina cement, first into an electrideres and then into an electric conductor.^{7,13} Despite many attempts just ten electrideres have been synthesized,^{4,5,9} only three of them being stable at room temperature. The density of the free electrons in electrideres is not large enough to be located in the X-ray of the crystal structure and its experimental characterization can only be achieved from indirect evidences.^{14–16} Thus far, only a few studies attempted the analysis of the electronic structure of these compounds and none featured the possibility of electrideres beyond the solid lattice, where the electron is hosted in an empty cavity.^{17,18} Different computational techniques were used to characterize electrideres, but no one presented a tool to unambiguously differentiate electrideres from other similar species. For instance, electrideres were shown to exhibit large non-linear optical properties (NLOP),^{19–21} non-nuclear attractors (NNA) of the electron density^{9,18} and even electron localization function (ELF) basins.^{9,22} However, other molecules show these properties without the presence of an isolated electron. This work has a twofold purpose: show that *molecular electrideres* can exist, and provide a means to characterize and distinguish them from

other similar species, thus contributing to the design of new electrideres. Finally, we will analyze whether the electrideres' structure truly consists of an isolated electron or it is actually just a formal picture to represent these molecules.

We will address seven molecules that have been previously labeled as electrideres and can be classified into three different groups: (i) *push electrideres*, where electron donor groups push the electron away from an alkali metal: tetracyanoquinodimethane (TCNQ) derivatives TCNQLi_2 and TCNQNa_2 ,²³ $\text{Li@calix[4]pyrrole}$ ^{20,24} and $\text{Li}\cdots\text{NCH}$;²⁵ (ii) *pull electrideres*, where electron withdrawing groups pull the electron away from an alkali metal: $\text{Li@B}_{10}\text{H}_{14}$ ²⁶ and $\text{Li}\cdots\text{HCN}$;²⁵ and (iii) *non-alkali electrideres*, where the electrideres structure holds an extra electron without the presence of a nearby alkali metal: $\text{e}^-@\text{C}_{60}\text{F}_{60}$.²¹ All these molecules show large NLOP,¹⁹ delocalized diffuse excess electrons on high-lying occupied orbitals and, therefore, they were previously characterized as electrideres.^{20,21,23,25,26} To study these compounds, *ab initio* calculations at the B3LYP level with split-valence double-zeta basis sets augmented with polarization and diffuse functions have been performed in conjunction with quantum theory of atoms in molecules (QTAIM)²⁷ and ELF analyses²⁸ (see ESI[†] for details).^{29–33} All the molecules presented in this work show ionization potentials above 3.82 eV.[†] The characterization of an electrideres will be performed using three different criteria that are consistent with the presence of an isolated electron: the existence of a NNA, an ELF basin, and negative values of the Laplacian of the electron density ($\nabla^2\rho$). NNA are maxima of the electron density at points distinct from nuclear positions; ELF basins are molecular regions with highly localized electrons; and $\nabla^2\rho$ basins were proposed as a physical basis for the valence-shell electron-pair repulsion (VSEPR) model.²⁷ Some of these criteria have been used in the past to characterize electrideres,^{9,18,22} but the occurrence of only one criterion is not a sufficient condition to assess the presence of an electrideres. Indeed, NNAs and negative values of the Laplacian are found in species such as C_2H_2 ,³⁴ ELF basins are usually present in valence regions of molecules such as HCN, while systems like polydiacetylene show large NLOP. None of these molecules is an electrideres and, therefore, none of the mentioned criteria by itself is valid to unambiguously characterize an electrideres. Yet electrideres usually show some of these

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properties.^{9,18} Do electrides need to fulfill all these criteria or only a small subset of them?

The first molecules submitted to analysis are TCNQLi₂ and TCNQNa₂. These molecules contain the TCNQ moiety, which acts as an electron acceptor in a number of charge-transfer complexes. The two alkali metals are close to the nitrogen lone pairs that push electron density from the metals, giving rise to an isolated electron hold by the electrostatic forces exerted by two positively-charged metals (see Fig. 1). The QTAIM analysis of TCNQLi₂ shows a NNA between both Li core basins with a negative value of $\nabla^2\rho$. There are 0.7 electrons in the NNA basin (68% of them completely localized in this region) and an ELF basin between the metals with 0.89 electrons. This data clearly indicates the presence of an isolated electron between the lithium atoms. This situation is reminiscent of the Li₂, where a NNA is also located in the center of the bond, there is an ELF basin and the molecule exhibits a large second hyperpolarizability.^{35,36} In this sense, TCNQLi₂ could be regarded as a molecular realization of Li₂, which is a strong electrophile and, therefore, difficult to handle. TCNQNa₂ analysis provides a similar picture. These results are confirmed by more accurate calculations at the MP2 and CISD levels of theory. The details of these calculations and the analogous analysis of the TCNQNa₂ species are included in the ESI.[†]

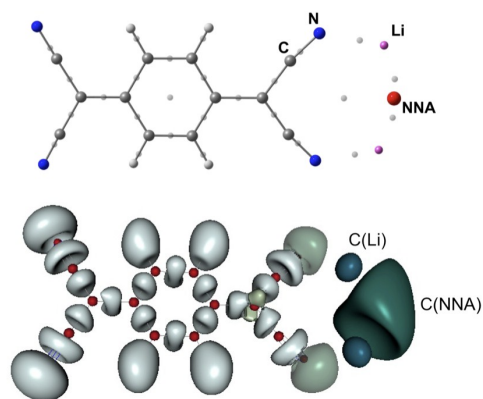


Fig. 1 QTAIM topological analysis (top) and ELF=0.75 (bottom) representations of TCNQLi₂.

Li@calix[4]pyrrole (Fig. 2) possesses a cup-shaped structure with a lithium atom lying in the narrowest region of the cup. The lone pairs of the nitrogen atoms of the pyrrole rings push the electron away from the alkali metal, leading to an electride-like structure. This picture is corroborated by the finding of a NNA and an ELF basin below the lithium region, where there is also a negative Laplacian value. However, the electron numbers of these basins (0.17e and 0.51e, respectively) are not fully consistent with the formal electride structure of almost one electron isolated from the rest of the

molecule. Furthermore, the electron density on this region is quite delocalized, with only 0.02 and 0.34 electrons localized in the NNA region and the ELF basins, respectively.

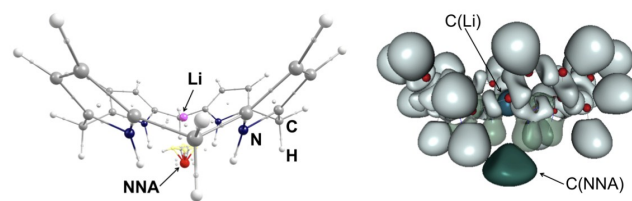


Fig. 2 QTAIM topological analysis (left) and ELF=0.75 (right) representations of Li@calix[4]pyrrole.

Li@B₁₀H₁₄ is formed by a nido boron hydride cluster with a lithium atom on top of the open cavity (see Fig. 3). The mechanism to hold the alkali metal is the complete opposite of previous molecules. The electron-deficient decaborane cluster exerts an attractive force on the electron density of the lithium that pulls the electron away from the alkali and holds it encapsulated in the box. This picture suggests that a NNA and an ELF basin should be located in the center of the cage but none is found. The analysis of the Laplacian of the electron density does not reveal any important contributions either. Therefore, we cannot characterize this molecule as an electride despite the large values of the first hyperpolarizabilities reported.²⁶ The latter is due to the highly delocalized nature of this molecule, which has up to 36% of its electron density delocalized, including the four uppermost hydrogen atoms of the cluster that delocalize 0.5e between them or towards the lithium atom.

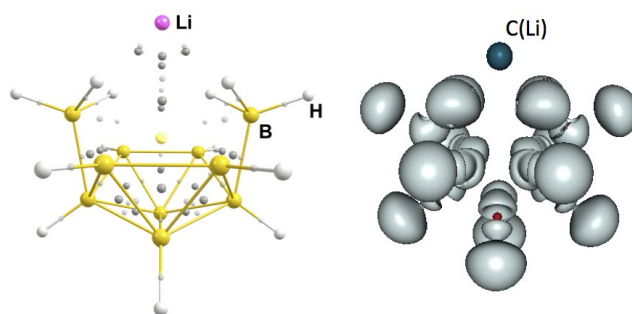


Fig. 3 QTAIM topological analysis (left) and ELF=0.75 (right) representations of Li@B₁₀H₁₄.

Hydrogen cyanide can interact with a lithium atom from both ends of the molecule to give Li···HCN and Li···NCH (see Fig. 4). The latter was suggested a push-electride, where the lone pair of nitrogen atom plays the usual role of pushing electrons away from lithium, generating an isolated electron at one extreme of the molecule.²⁵ Li···HCN was also predicted to have an electride-like structure, but as a result of the opposite mechanism: the internal polarization of hydrogen cyanide

induces a partial positive charge over the hydrogen atom that can withdraw electron charge from lithium, giving rise to an isolated electron between HCN and the alkali metal. The QTAIM analysis does not reveal any NNA for either species but the ELF analysis does find valence basins in the proximity of lithium. However, these basins remain so close to lithium that can be barely considered anything else than the lithium valence itself. The examination of the Laplacian of the electron density leads to the same conclusions drawn from the ELF study. Therefore, the analyses describe these molecules as a lithium atom perturbed by the presence of hydrogen cyanide, a picture that by no means is consistent with an electride as it was previously suggested.²⁵

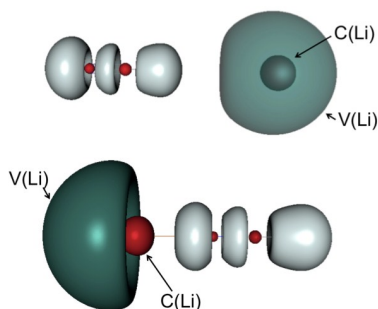


Fig. 4 ELF=0.75 representations of Li...HCN (top) and Li...NCH (bottom) molecules.

Finally, we will analyze the only *non-alkali electride* reported,²¹ which is not constructed by pulling or pushing electrons from alkali metals. The $e\text{-@C}_{60}\text{F}_{60}$ (Fig. 5) consists of a $\text{C}_{60}\text{F}_{60}$ cage with sufficient interior attractive potential to host an electron inside. We have performed additional calculations to assess the validity of this statement.[†] The topological analysis shows a NNA in the center of the cage and the corresponding ELF basin. These basins accommodate 0.19 electrons. The electronic structure of $\text{C}_{60}\text{F}_{60}^-$ is consistent with an electride-like molecule but it cannot be considered a formal one-electron electride. The analysis of the Laplacian of the electron density corroborates this hypothesis, giving negative values in the center of the cage. These results have been reproduced with different basis sets, ruling out the possibility of a basis set artifact.[†]

The results reported in this letter support the existence of gas-phase molecular electriles, thus extending the possibility of this species beyond the lattice. Only TCNQ-based molecules can be presented as *formal electriles*, with almost one electron isolated. Pyrrole-calixarenes and polarized hollow structures have also electronic features consistent with electriles, but their NNA basins contain far less than one electron. Thus these chemical systems may be also classified as electride-like molecules and are candidates to design new electriles. The table below summarizes these findings and re-

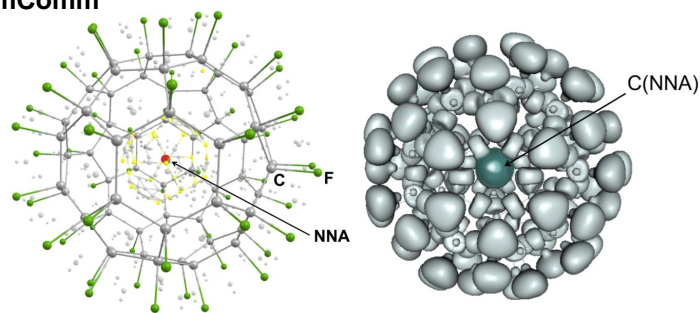


Fig. 5 QTAIM topological analysis (left) and ELF=0.75 (right) representations of $e\text{-@C}_{60}\text{F}_{60}$.

veals the criteria to identify electriles.

All the molecules studied in this manuscript were previously considered electriles on the basis of large NLOPs and frontier orbitals with large density values in the vicinity of the position where one would expect the isolated electron of the electride. However, we have shown here that some of them are actually not electriles. The presence of a NNA, an ELF basin or negative values of the Laplacian of the electron density are necessary conditions to assert the existence of an isolated electron. Nevertheless, molecules such as C_2H_2 , with a NNA or the ELF basin close to an atomic position, put forward that these conditions might not be always sufficient to assess the presence of an electride. In this respect, large NLOPs can be used together with the latter conditions to confirm the true electride nature of a given species.

NNA are not a frequent feature of molecular densities. Therefore, one could design an electride by prompting the occurrence of a NNA using the data of Pendás and coworkers,³⁴ who analyzed the range of diatomic distances at which several dimers show a NNA. The TCNQ actually plays the role of stabilizing Li_2 and Na_2 molecules at a favorable distance where the NNA appears. We hope that our results will motivate further research on this fascinating species and the development of new electriles with compelling applications.

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Table 1 Summary of the criteria used to characterize electrides in this study. * These molecules show NNA, $\nabla^2\rho$ or ELF basins in the close vicinity of an atom and, therefore, the isolated nature of the electron is dubious.

| | NLOP | NNA | $\nabla^2\rho$ | ELF | Electride? |
|------------------------------------|------|-----|----------------|-----|------------|
| TCNQLi ₂ | ✓ | ✓ | ✓ | ✓ | ✓ |
| TCNQNa ₂ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Li@calix[4]pyrrole | ✓ | ✓ | ✓ | ✓ | ✓ |
| Li@B ₁₀ H ₁₄ | ✓ | × | × | × | × |
| e-@C ₆₀ F ₆₀ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Li···HCN | ✓ | × | ✓* | ✓* | × |
| HCN···Li | ✓ | × | ✓* | ✓* | × |
| Li ₂ | ✓ | ✓ | ✓ | ✓ | ✓ |
| C ₂ H ₂ | × | ✓* | ✓* | ✓* | × |

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