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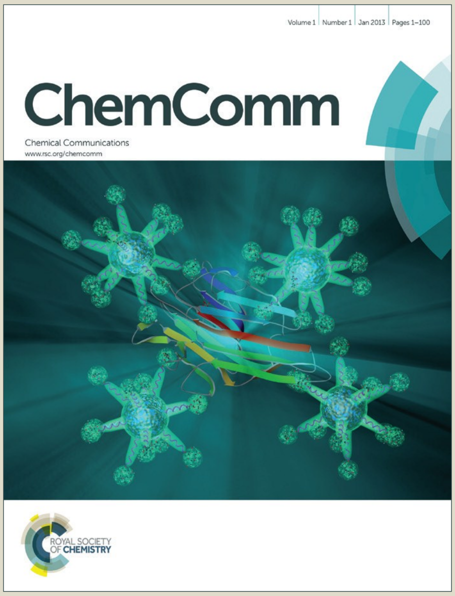

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On the existence of intramolecular one-electron Be-Be bonds.

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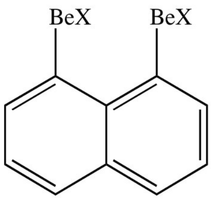
Although Be-Be bond is extremely weak in Be_2 dimers, we have shown that rather stable Be-Be one-electron sigma bonds are formed upon electron attachment to 1,8-diBeX-naphthalene derivatives. Wavefunction analyses corroborate the formation of Be-Be covalent linkages in which the extra electron is accommodated between the Be atoms as reflected in a dramatic shortening of the Be-Be distance with respect to the corresponding neutral molecule.

The possible existence of Be_2 molecules attracted the interest of chemists for many years, since the MO theory predicts for this element a behavior similar to the noble gases, where no neutral stable diatomic molecules should be formed.[1-10] However, the existence in Be of close lying empty *2p* orbitals opens the possibility of an energetically feasible *sp* hybridization, not possible for noble gases, and therefore the possibility of forming stable derivatives as BeH_2 or $BeCl_2$. But still the existence and stability of Be_2 molecules was an open question along many years. Back in 1984, the first evidences of the existence of Be_2 in the gas phase were reported in the literature,[11,12] though the dissociation energy of this dimer was extremely small (11 $kJ \cdot mol^{-1}$).[13-15] For many years the nature of the bonding between two Be atoms remained unknown, until recent high-level ab initio calculations showed that the bonding is essentially due to non-dynamical correlation effects which mix two quasi-degenerate orbitals with a rather low occupancy.[16] However, Be is an electron deficient system and beryllium derivatives behave as very strong Lewis acids, when interacting with a great variety of Lewis bases, yielding rather strong linkages, named beryllium bonds.[17] The formation of beryllium bonds actually triggers a significant distortion of the BeX_2 compound, which departs significantly from linearity, because the electron density is accepted into the empty *p* orbitals of Be, what necessarily results in a change of its hybridization from pure sp to sp^n ($1 < n \leq 2$).[17] This intrinsic acidity of -BeX groups also leads to the formation of intramolecular beryllium bonds, provided that within the same molecule a Lewis-basic center able to interact with a -BeX group exists.[18] When two -BeX groups coincide in the same compound, one should not expect them to interact in a bonding manner due to the aforementioned electron-deficient character, but they could still behave as very good electron acceptors. The question we have tried to address in this communication is what would be the electronic structure of such kind of systems after accepting an extra electron. If both -BeX groups are physically close, very likely the extra electron should be trapped between both electron-deficient Be-X groups. Is this indeed the case? To answer this question we have considered as appropriate candidates 1,8-disubstituted naphthalene derivatives in which the substituents at positions 1 and 8 are BeX (X = H, F, Cl, Br, CH_3 NH_2, OH, CF_3, $C(CF_3)_3$, NF_2, OF, CN, NO_2, SOH, *t*-Bu, Ph) groups (see Scheme 1). We will show, through the use of high-level ab initio and density functional theory (DFT) calculations that, indeed in most cases, although in not all of them, the global minimum of the corresponding radical anion is stabilized through the formation of a rather strong one-electron σ Be-Be bond.

For this purpose, the structures of the neutral 1,8-disubstituted naphthalene derivatives and of their radical anions have been fully optimized at the B3LYP/6-31+G(d,p)



Scheme 1. 1,8-disubstituted naphthalene derivatives included in this study. X = H, F, Cl, Br, CH_3, OH, CF_3, $C(CF_3)_3$, $N(CH_3)_2$, OCH_3, NF_2, OF, CN, NO, $SOCH_3$, *t*-Bu, Ph.

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Electronic supplementary information (ESI) available: Geometrical details, electron affinities, other energetic data, molecular graphs and ELF plots. See DOI: 10.1039/x0xx00000x

level of theory. The same approach was used to obtain the harmonic vibrational frequencies, which confirm that all the structures reported correspond to local minima of the corresponding potential energy surfaces. In order to have more reliable relative energies, the final total energies have been obtained using the same B3LYP functional but with a much extended 6-311+G(3df,2p) basis set. This theoretical model was assessed by comparing the B3LYP optimized structures with those obtained at the CCSD(T)/cc-pVDZ level of theory, for the anions in which X = H, F, as suitable model systems. As shown in Figure S1 of the supporting information the agreement between both sets of values can be considered as excellent, in particular in what concerns the interaction involving both Be atoms. Also importantly, the relative stability of the two isomers does not change on going from the B3LYP to the CCSD(T) calculation. We have also verified that the structure of these systems does not change appreciably when using multireference CASSCF methods(see Figure S2 of the supporting information), confirming that these kind of systems are well described by methods accounting for electron correlation effects, but based on a single configuration, such as MP2, CCSD(T) or G4 theory. Finally, we have also verified that when a more flexible cc-pVTZ basis set is used the effect on the optimized structures is marginal (see Figure S3 of the supporting information, and the corresponding discussion). Three different approaches, namely the Atoms in Molecules (AIM) theory,[19] the Natural Bond Orbital (NBO) method[20] and the Electron Localization Function (ELF)[21] have been used to analyze the bonding in the systems under investigation, and to confirm the formation of one-electron Be-Be bonds upon electron attachment.

In principle, the neutral 1,8-disubstituted naphthalene derivatives may have different conformations depending on the relative position of the -BeX groups with respect to the aromatic rings (See Figure 1). However for the parent compound (X = H) as well as for two other derivatives chosen as suitable examples (X = F, CN), the most stable one corresponds to the conventional structure **1** in which the Be atom and the central atom of the substituents X lay on the plane of the naphthalene ring. The other local minima are higher in terms of free energy (see Table S1 of the supporting information), so we can conclude that the most stable structure for 1,8-disubstituted naphthalene derivatives corresponds to the conventional conformation **1**.

The attachment of one electron to these three kind of conformations lead to the three anions shown in Figure 2, namely **A1**, **A2** and **A3**. The first conspicuous fact is that electron attachment to structures of type **1** leads to anions in which the Be-Be distance decreases dramatically. The formation of **A2** and **A3** anions, on the contrary does not entitle significant structural changes with respect to the corresponding neutrals, in particular in what concerns the Be-Be distance that actually lengthens slightly rather than shortening. On the other hand only **A1**- and **A2**-type structures are found to be minima of the potential energy surface, whereas all the **A3**-type structures are predicted to be transition states, whose imaginary frequency corresponds to a vibrational mode that would connect two identical **A1** minima in which the positions of the BeX groups are interchanged. The most important finding however is that for the majority of the substituents the anion formed from the most stable neutral, **A1**, is also the most stable anionic species (See Table S3 of the supporting information). For X = H, CH_3, CF_3, *t*-Bu, Ph, however the **A2** anion is slightly more stable than **A1** in terms of free energies (see Table S3). However, it should be remembered that also in these cases the dominant neutral structure is predicted to be of the **1**-type, and therefore, electron attachment should produce **A1**-type structures, that would eventually isomerize to the most stable **A2**-type anions. However, the activation barrier associated with such a process is rather high (81 kJ·mol^{-1} in terms of free energies for X = H) and therefore even in the aforementioned cases in which the **A2** structure is found to be slightly more stable than the **A1** one, the isomerization would not occur under normal conditions because of the high activation barriers involved. Hence, one should expect, no matter the nature of the substituent, that electron attachment should produce **A1**-type structures in all the cases.

Let us now analyze in more detail the bonding in **A1** anions. The most significant finding, as mentioned above, is the significant shortening of the Be-Be distance (See Table 1), pointing to a significant bonding pattern change on going from the neutral system to the anion. This shortening is particularly dramatic for X = *t*-Bu and $C(CF_3)_3$ because these bulky substituents force the Be-Be distance to be very large in the neutral system, whereas in the anion, the formation of the one-electron Be-Be bond (vide infra) leads always to Be-Be distances around 2.3 Å independently of the nature of the X substituent. Note that these Be-Be distances are only 0.3 Å longer than normal (two-electron) Be-Be bonds as the one in

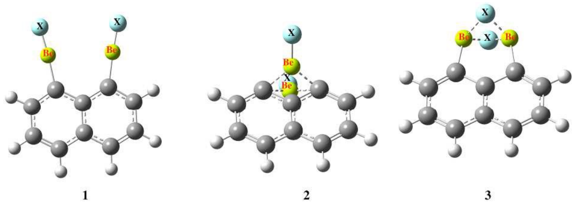


Figure 1. Different types of local minima of neutral 1,8-diBeX derivatives of naphthalene. Type 1 structures were found to be the global minimum in all cases investigated.

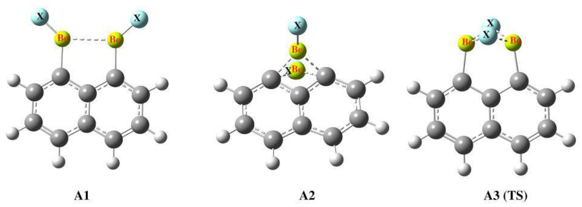


Figure 2. Different stationary points of the radical anions of 1,8-diBeX derivatives of naphthalene. Structures **A3** are found to be transition states rather than local minima.

FBe–BeF[22] (see also Table S2 of the supporting information). This shortening is consistent with the existence of a Be-Be stretching displacement around 250-330 cm^{-1}. It is also very important to emphasize that whereas G4 calculations[23] predict a positive electron affinity for naphthalene (7.5 kJ·mol^{-1}, so the anion should not exist), for the 1,8-diBeX derivatives investigated the calculated electron affinity of the corresponding neutral systems goes from -53.7 (X = OCH_3) up to -220.3 kJ·mol^{-1} (X = $C(CF_3)_3$) (see Table S4 of the Supporting Information). The existence of this stabilizing Be-Be interaction is also reflected in the molecular graphs of the **A1**-anions which show the existence of a Be-Be bond critical point (see Figure 3 and Figure S4 of the Supporting Information), with an electron density that is typically around 0.033 a.u (see Table 1) that does not exist in the neutral compounds.

Table 1. Shortening of the Be-Be internuclear distance (ΔR(Be-Be)) upon electron attachment; electron density at the Be-Be bond critical point; character of the hybrids involved in the one-electron Be-Be bond, together with its electron population and the corresponding Wiberg bond order (WBO).

X	ΔR (Be-Be) (in Å)	ρ_{BCP} (a.u.)	Hybrids character	Electron population	WBO
H	0.676	0.033	s(78.4%) p 0.27(21.5%)	0.922	0.195
F	0.667	0.033	s(79.6%) p 0.25(20.2%)	0.932	0.235
Cl	0.801	0.036	s(78.8%) p 0.27(21.1%)	0.937	0.226
Br	0.843	0.038	s(78.5%) p 0.27(21.4%)	0.937	0.223
CH_3	0.645	0.032	s(81.3%) p 0.23(18.6%)	0.884	0.189
OH	0.538	0.030	s(80.9%) p 0.23(19.0 %)	0.929	0.230
CF_3	0.607	0.035	s(81.9%) p 0.22(18.0%)	0.893	0.200
$C(CF_3)_3$	1.243	0.033	s(78.7%) p 0.27(21.2%)	0.875	0.215
$N(CH_3)_2$	0.633	0.032	s(80.7%) p 0.24(19.2%)	0.884	0.206
OCH_3	0.569	0.031	s(81.8%) p 0.22(18.1%)	0.911	0.223
NF_2	0.849	0.035	s(79.6%) p 0.25(20.3%)	0.879	0.202
OF	0.578	0.034	s(81.2%) p 0.23(18.7%)	0.870	0.202
CN	0.883	0.034	s(80.9%) p 0.23(19.0%)	0.852	0.173
NO[a]	-	-	-	-	0.030
SOMe	0.597	0.034	s(81.4%) p 0.23(18.5%)	0.928	0.233
t-Bu	0.926	0.033	s(82.1%) p 0.22(17.8%)	0.883	0.204
Ph	0.741	0.033	s(82.5%) p 0.21(17.4%)	0.854	0.182

[a] For X = NO both neutral and anion can be seen as the result of the interaction between a $(NO)_2$ dimer and the $C_{10}H_6Be_2$ moiety, so no Be-Be is formed (see Figure S4 of the supporting information).

Furthermore, as shown also in Figure 3 both the energy density and the Laplacian of the energy density at the Be-Be BCP are always negative indicating that this interaction has a non-negligible covalent character, also confirmed by the ratio –G(r)/V(r) which is typically around 0.14.[24] This is totally consistent, also, with the description of the bonding provided by the NBO analysis, which shows the existence, in all cases of a Be-Be bonding molecular orbital with a large contribution of the 2s orbitals of Be (around 80%), and with a population always around one electron, and which, as illustrated in the second row of Figure 3 is totally localized between the two Be atoms. Also consistently, the Wiberg bond order (WBO)[25] is not negligible (See Table 1). These two pictures are in harmony with the one that can be obtained by means of the ELF approach. Indeed, as it is clearly illustrated in the third row of Figure 3 (see also Figure S5 of the Supporting Information), in all the **A1**-type anions, a Be-Be disynaptic-basin is systematically located, with a population always around one electron, ratifying that **A1**-type anions are stabilized through the formation of one-electron Be-Be bond.

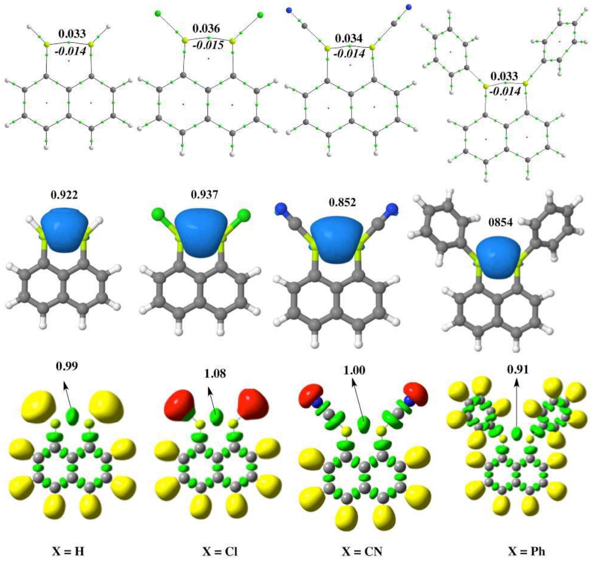
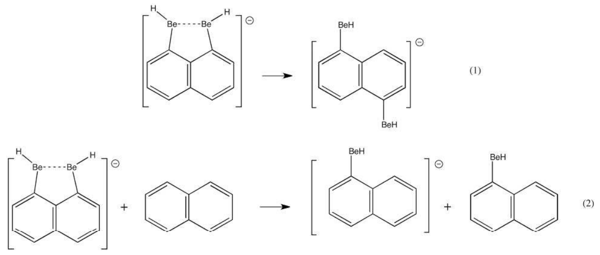


Figure 3. Molecular graphs (first row) for 1,8-diBeX-naphthalene radical anions (X = H, Cl, CN, Ph). Green and red dots correspond to bond and ring critical points respectively. For the Be-Be bond critical point the electron density, its Laplacian (in red) and the energy density (in italics) are given. Both values in are a.u. The second row shows the one-electron localized MO between both Be atoms obtained through the NBO approach. Its population is also given. The third row presents the ELF plots for the same systems. Yellow lobes correspond to disynaptic basins involving hydrogen atoms. Green lobes correspond to disynaptic basins between heavy atoms and red basins denote monosynatic basins associated with lone-pairs**.** The population (e-) of the Be-Be disynaptic basin is shown.

It is also worth mentioning that in **A2**-type isomers, there are no Be-Be bonds. As illustrated by the corresponding molecular graphs the two Be atoms bridge between C1 and C8 of the naphthalene molecule, but no BCP is found between both Be atoms (see Figure S6 of the Supporting Information).

In order to have an idea of the strength of this one-electron linkage we have used the two isodesmic reactions shown in Scheme 2. In order to ensure the reliability of these estimates, the calculation of the reaction energies was carried out at the G4-level of theory, which typically yields values with errors smaller than 4 kJ·mol^{-1}.

The energetics also confirms the existence of these one-electron Be-Be bonds. The Localized Molecular Orbital Energy Decomposition Analysis (LMOEDA)[26] (see details in the supporting information) show that in the 1,8-diBeX-naphthalene radical anions, the Be-Be interaction exhibits a significant covalent character. Consistently, G4 theory predicts the isodesmic reaction (1) of Scheme 2 to be endothermic by 61 kJ·mol^{-1}. This value, which can be taken as a reasonable estimate of the strength of the one-electron Be-Be in the **A1** anion for X = H, should be corrected by the energy change of



Scheme 2. Isodesmic reactions to estimate the energy of the one-electron Be-Be bond.

the C-Be bonds, which in the reactants are weaker than in the products. Our estimate of this effect is 15 kJ·mol^{-1} (see Table S5 of the Supporting information) what would yield for the energy of the Be-Be bond 76 kJ·mol^{-1}. The value obtained when reaction (2) is used is 89 kJ·mol^{-1}, so we can infer that the energy associated with this one-electron Be-Be sigma bond for the parent compound (X = H) is typically around 80 kJ·mol^{-1}, and it should be slightly stronger for electron withdrawing substituents. Again these values are consistent with those obtained in our LMOEDA analysis, which gives for the Be-Be bond in the $[(CH_3BeH)_2]^-$ dimer an energy of -74 kJ mol^{-1} (see details in the Supporting Information) It can then be concluded that even though a direct interaction between two Be atoms leads to an extremely weak bond, rather stable one-electron Be-Be bonds similar to B-B bonds recently reported in the literature[27,28] are formed upon electron attachment to 1,8-diBeX-naphthalene derivatives, showing that this property can be considered a signature of this kind of compounds when they involve electron deficient atoms as substituents. Finally it is worth noting the formal similarity between 1,8-diBeX-naphthalene derivatives and proton sponges such as 1,8-Bis(dimethylamino)naphthalene.[29] The latter interact strongly with protons through the Lewis base $N(CH_3)_2$ substituents, whereas the former do it with electrons through the Lewis acid BeX substituents.

Acknowledgments

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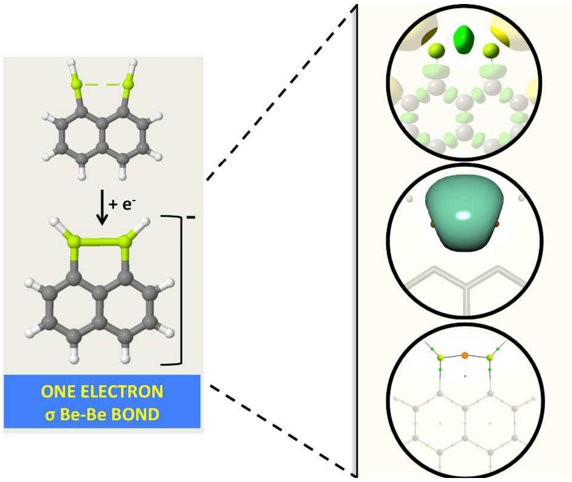

The electron attachment to 1,8-diBeX-naphthalene derivatives leads to rather stable radical anions through the formation of one-electron Be-Be bonds.