On the existence of intramolecular one-electron Be-Be bonds.
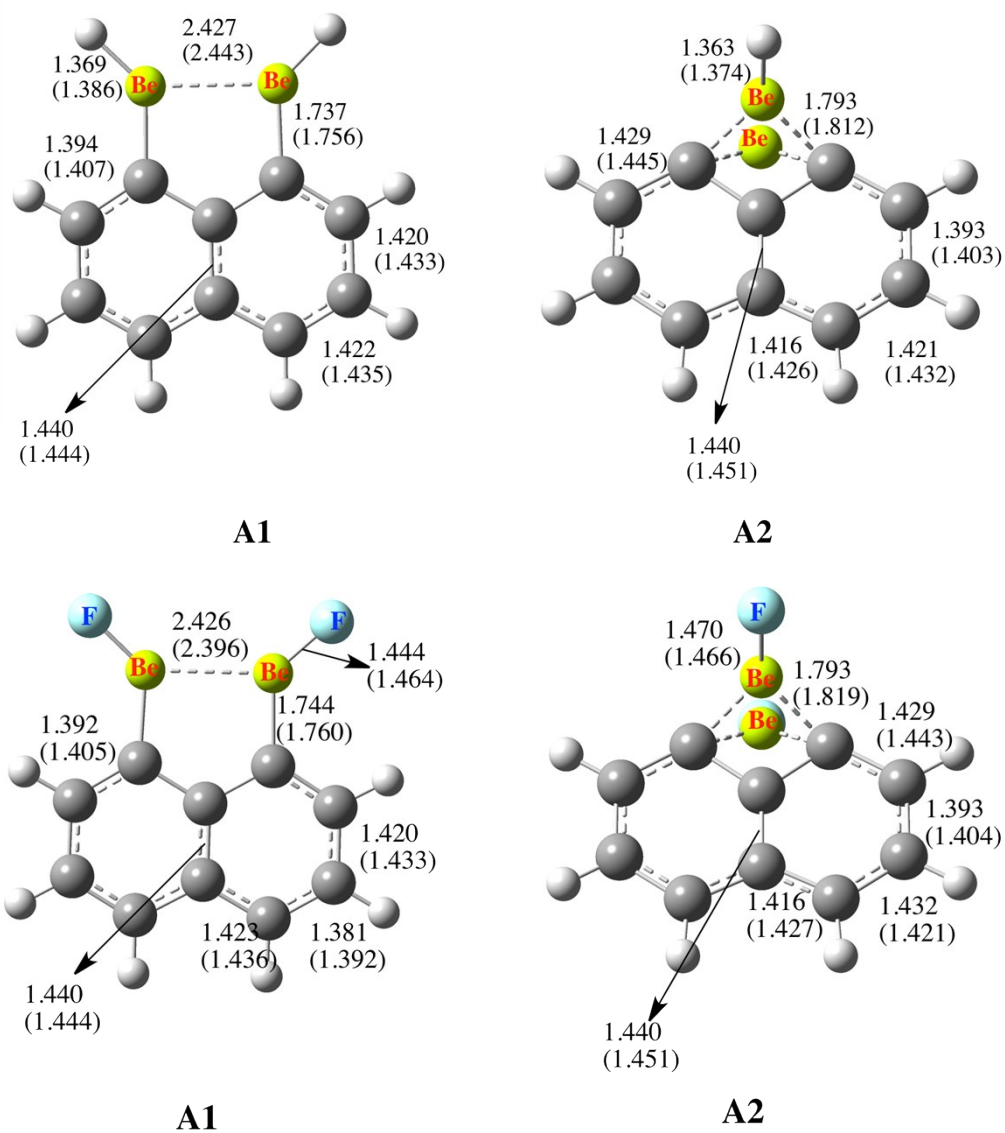
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**Supporting Information (A total of   11 pages)**

Figure S1. Comparison between B3LYP/6-31+G(d,p) and CCSD(T)/cc-pVDZ (values within parenthesis) optimized geometries of the stable anions of 1,8-BeX-naphthalene derivatives (X = H, F). Bond lengths in Å. In spite of the fact that in isomers **A2** the Be-Be distances are around 2.2 Å, in both cases, no bond critical point is found between both Be atoms.
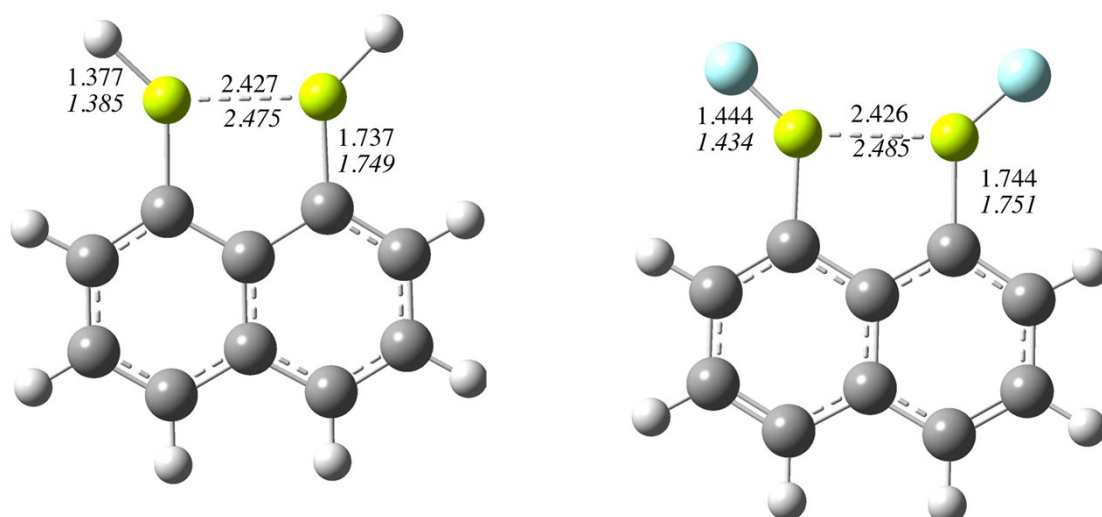
Figure S2. Comparison of the optimized geometrical parameters which characterize the formation of the one-electron Be-Be bond in 1,8-BeX-naphthalene anions (X = H, F), obtained through B3LYP/6-31+G(d,p) and CASSCF(5,6)/6-31+G(d,p) calculations. The latter are written in italics.

Basis set effects

The effect on enlarging the size of the basis set on the structural characteristics of the one-electron Be–Be bonds was investigated at two different levels of theory. In the first assessment, we have compared the structures obtained when a B3LYP/6-31+G(d,p) theoretical model is used with those obtained at the B3LYP/cc-pVTZ level, for some 1,8-BeX-naphthalene anionic derivatives, taken as suitable examples (see Figure S3a). The second assessment was done using high-level ab initio methods. Taking into account that geometry optimizations at the CCSD(T)/cc-pVTZ are too expensive for systems of the size consider in this study, this assessment was made by using the RI-CC2 method, in which only singles and doubles excitations are taking into account. The results of this comparison are shown in Figure S3b.


(a)

(b)
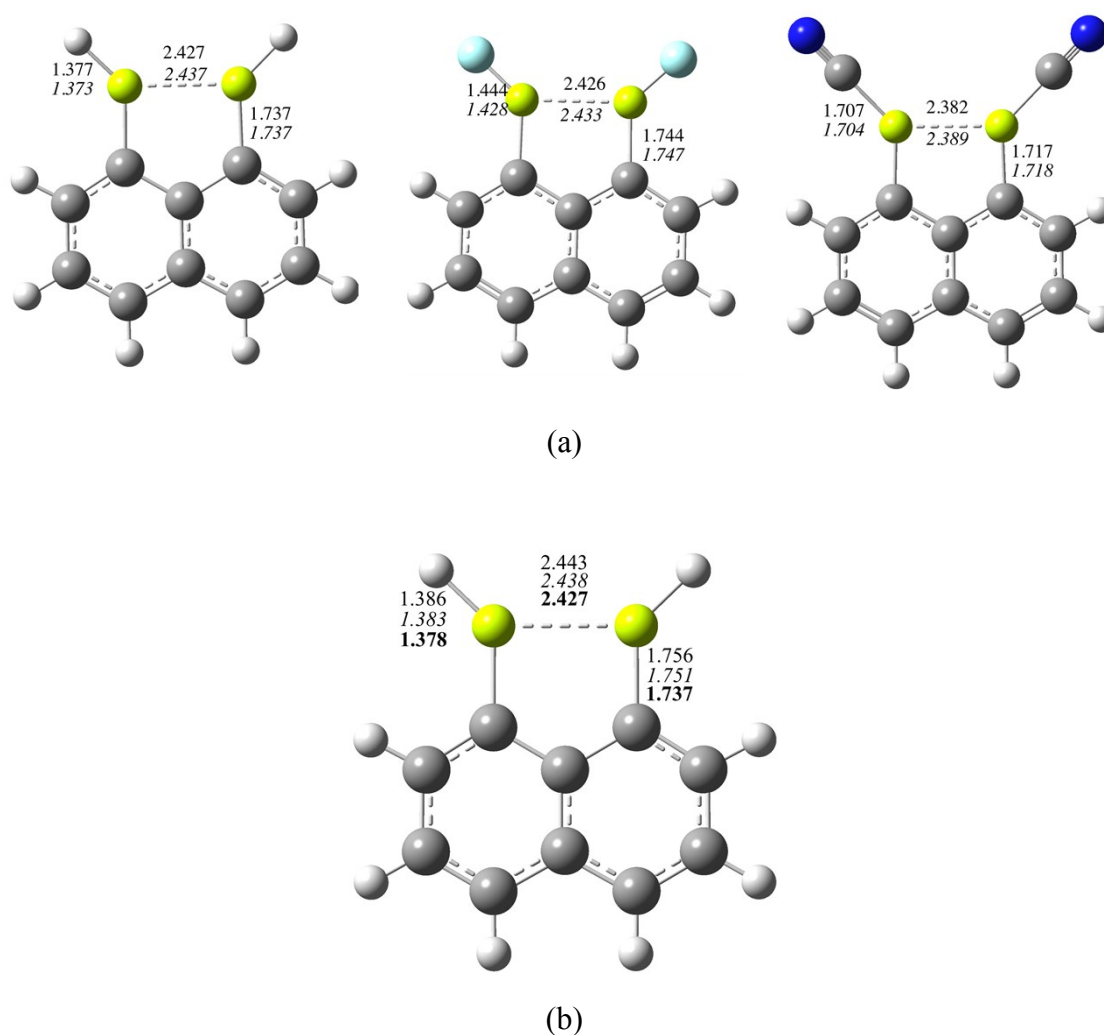
Figure S3. (a) Effect of enlarging the basis set from a split-doule zeta 6-31+G(d,p) to a triple zeta cc-pVTZ on the geometrical parameters associated to the existence of a Be-Be one-electron bond, when the B3LYP hybrid functional is used. Values in italic correspond to those obtained with the cc-pVTZ basis set expansion. **(b)** Comparison between CCSD(T)/cc-pVDZ geometrical parameters, with those obtained at the RI-CC2/cc-pVDZ (italic) and at the the RI-CC2/cc-pVTZ (bold) levels of theory, respectively.
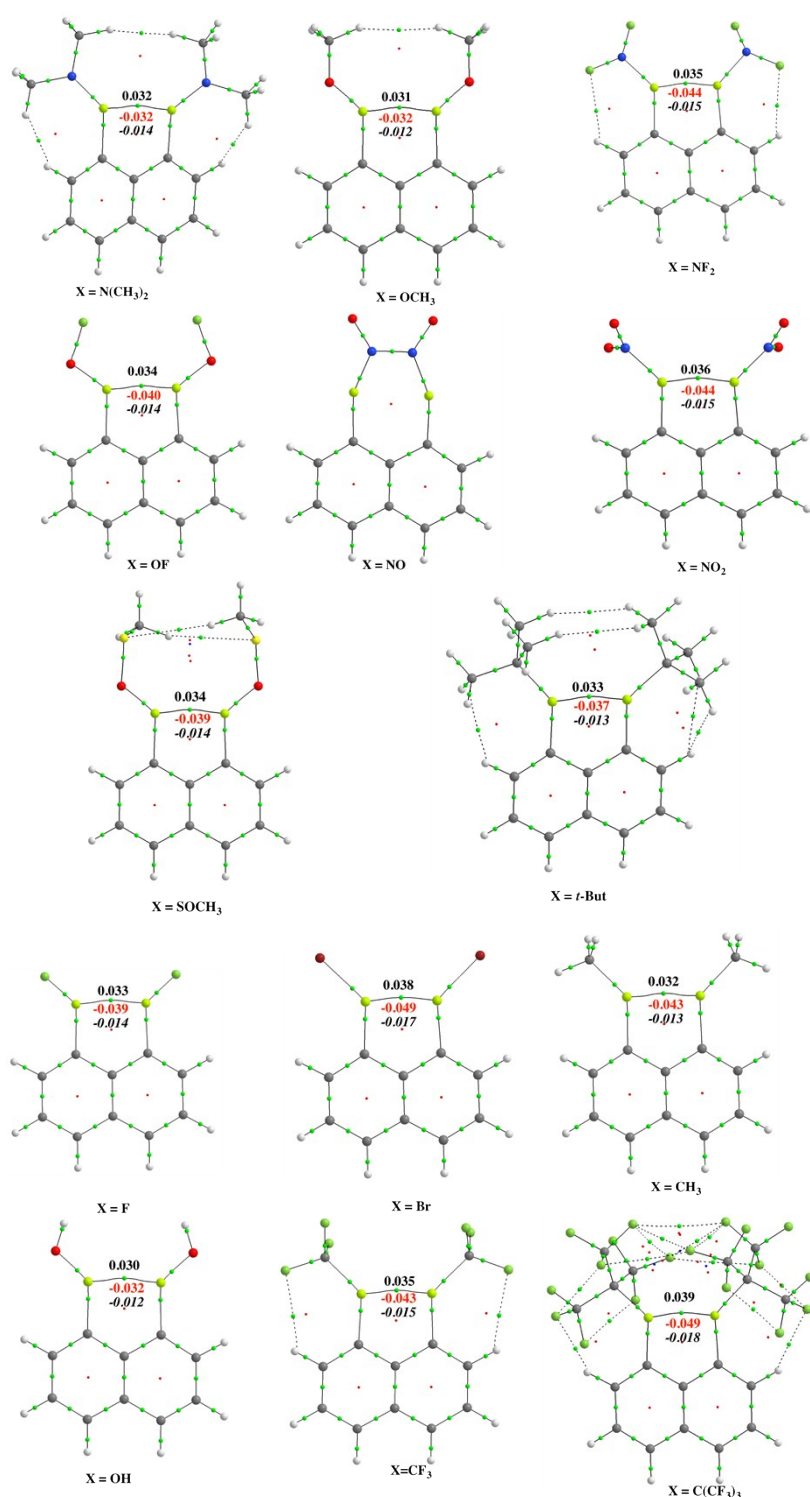
Figure S4. Molecular graphs for 1,8-BeX-naphthalene **A1**-type anions (X = F, Br, CH₃, OH, CF₃, C(CF₃)₃, N(CH₃)₂, OCH₃, NF₂, OF, NO, NO₂, SOCH₃, *t*-But), showing the existence of a one-electron Be-Be bond, with the only exception of X =NO, where the systems is stabilized through a N-N bond between the two substituents. Green and red dots correspond to bond and ring critical points respectively. For the Be-Be bond critical point, the electron density and its Laplacian (in red) as well as the energy density (in italics) are given in a.u.
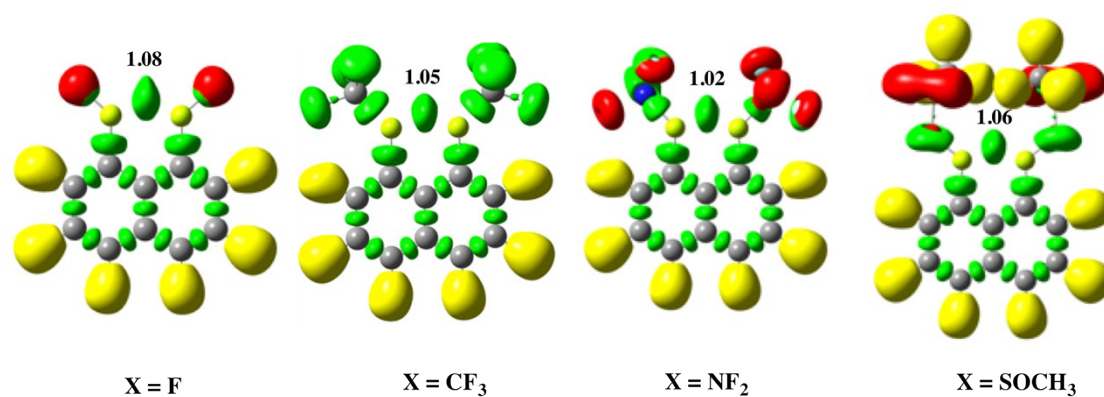
Figure S5. ELF plots for 1,8-BeX-naphthalene anions (X = F, CF_3, NF_2, $SOCH_3$). Yellow lobes correspond to disynaptic basins involving hydrogen atoms. Green lobes correspond to disynaptic basins between heavy atoms and red basins denote monosynatic basins associated with lone-pairs. The population (e-) of the Be-Be disynaptic basin is shown.
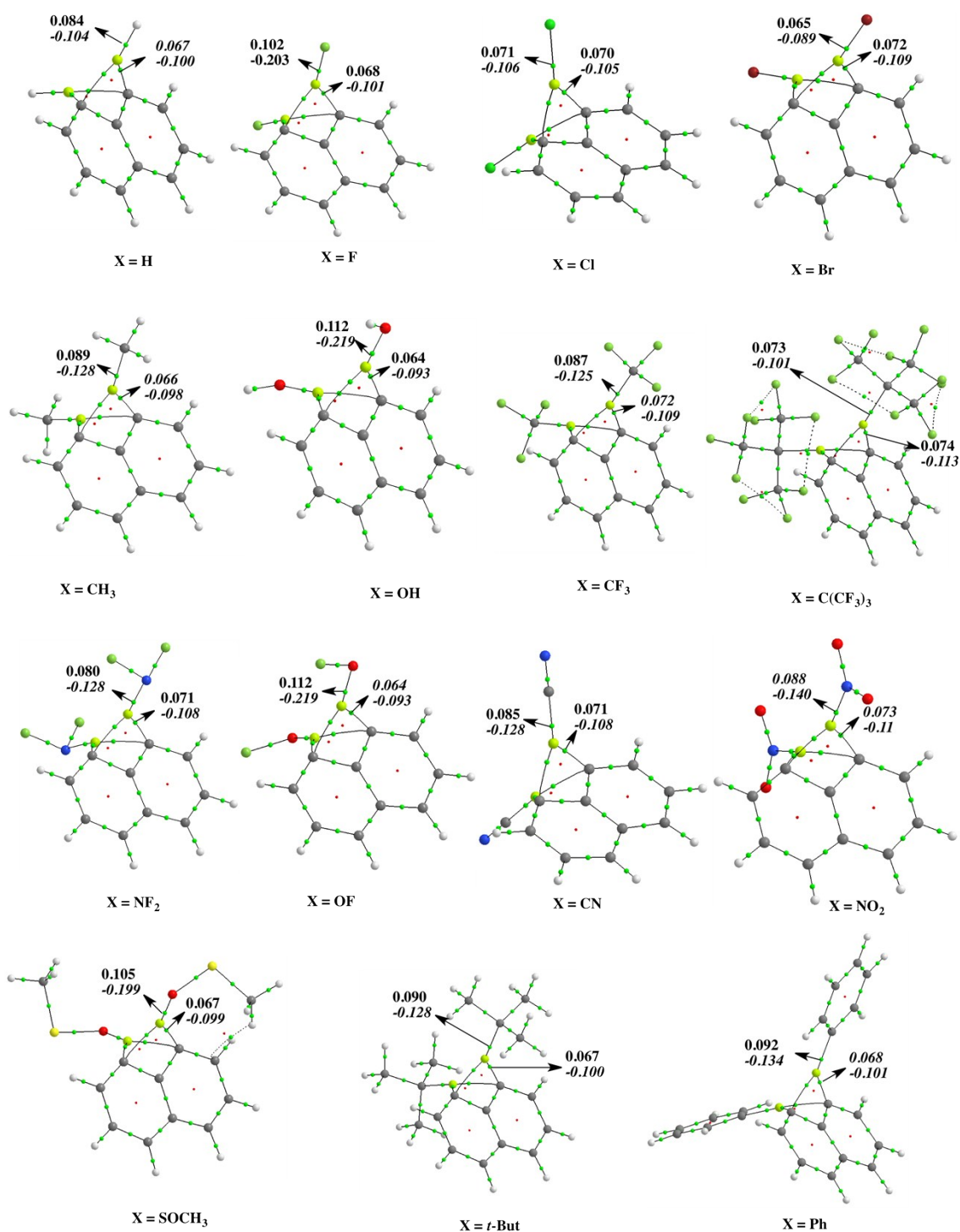
Figure S6. Molecular graphs for 1,8-BeX-naphthalene **A2**-type anions (X = H, F, Cl, Br, CH$_3$, OH, CF$_3$, C(CF$_3$)$_3$, NF$_2$, OF, CN, NO$_2$, SOCH$_3$, *t*-But, Ph). Green and red dots correspond to bond and ring critical points respectively. For the Be-Be bond critical point the electron density and the energy density (in italics) are given. Both values in a.u.

Table S1. B3LYP/6-31+G(d,p) relative free energy of isomers **2** and **3** with respect to isomer **1** minima for 1,8-BeX-naphthalene derivatives. Negative values (in kJ mol^{-1}), indicate that the corresponding isomer is more stable than isomer **1**.

X	Isomer 2	Isomer 3
H	36	40
F	55	56
Cl	185	223
Br	177	215
CF$_3$	208	143
N(CH$_3$)$_2$	-	49
OH	136	45
NF$_2$	75	16
OF	200	169
CN	5	93
NO	-	191

Table S2. Be-Be distances (Å) for 1,8-BeX-naphthalene derivatives and its anions

X	R (Be-Be) (neutral)	R (Be-Be) anion[a]
H	3.103	2.427
F	3.093	2.426
Cl	3.168	2.367
Br	3.172	2.329
CH$_3$	3.102	2.412
NH$_2$	2.979	2.418
OH	3.002	2.464
CF$_3$	2.978	2.371
C(CF$_3$)$_3$	3.548	2.305
NF$_2$	3.206	2.357
OF	3.370	2.375
CN	3.265	2.382
NO$_2$	3.161	2.344
SOH	3.008	2.312
t-Bu	3.369	2.443
Ph	3.156	2.415

[a] Note that these values are only ≈ 0.3 Å longer than normal (two-electron) Be-Be bonds as the one in FBe–BeF (G. Frenking et al. Angew. Chem. Int. Ed. 2016, doi:10.1002/anie.201601890). Note also that these distances are only slightly longer than those in Be_2^+ (2.246 Å) and Be_2^{2+} (2.130 Å) .

Table S3. B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) relative energy of **A2** with respect to **A1** minima for 1,8-BeX-naphthalene anions. Negative values (in kJ mol^{-1}) indicate that **A1** is more stable than **A2**

X	ΔH	ΔG
H	13.8	10.2
F	-20.3	-23.6
Cl	-10.6	-14.1
Br	-9.9	-10.9
CH$_3$	9.8	12.6
OH	-20.6	-24.1
CF$_3$	10.1	6.8
C(CF$_3$)$_3$	29.0	29.2
N(CH$_3$)$_2$	-0.9	-1.4
OCH$_3$	-20.8	-23.5
NF$_2$	-1.9	-3.0
OF	-5.5	-9.0
NO	-77.1	-63.5
CN	5.1	0.6
SOCH$_3$	-15.4	-15.4
t-But	19.0	14.9
Ph	10.9	8.3

Table S4. Electron affinity (EA, kJ mol^{-1}) of the 1,8-BeX-naphthalene derivatives investigated and Be-Be stretching frequency (υ_{BeBe}, cm^{-1}) of the corresponding **A1**-type anion.

X	EA (neutral)	υ_{BeBe} (anion)
H	-93.9	332
F	-99.8	278
Cl	-138.6	223
Br	-155.5	171
CH$_3$	-66.8	273
OH	-57.6	275
CF$_3$	-191.7	269
C(CF$_3$)$_3$	-220.3	301
N(CH$_3$)$_2$	-67	370
OCH$_3$	-53.7	247
NF$_2$	-137.9	156
OF	-148.3	275
NO	-124.0	313
CN	-214.7	198
SOCH$_3$	-93.9	256
t-But	-98.4	158
Ph	-106.5	131

Table S5. B3LYP/6-311+G(3df,2p) energies of 1,5-diBeH-naphthalene anion in its equilibrium conformation and with the C-Be distances equal to those of 1,8-diBeH-naphthalene anion.

R (C-Be)	E_{total} (a.u.)	ΔE (kJ·mol^{-1})
equilibrium	-415.5097376	0
1.737	-415.5040365	15

Localized Molecular Orbital Energy Decomposition Analysis (LMOEDA).

In order to characterize the Be-Be interactions in the anions under investigation, through the use of the LMOEDA,[a] we have considered two approaches. In the first one, we have taken the unsubstituted parent compound 1,8 BeH-naphthalene anion and we have define two different fragmentations. In fragmentation (a) we have define HBeBeH as a one of the fragments and the $C_{10}H_8$ moiety as another fragment. In fragmentation (b) we have taken only one of the BeH groups as the first fragment and $C_{10}H_8$BeH as the second fragment (see the following Scheme)

(a)   (b)
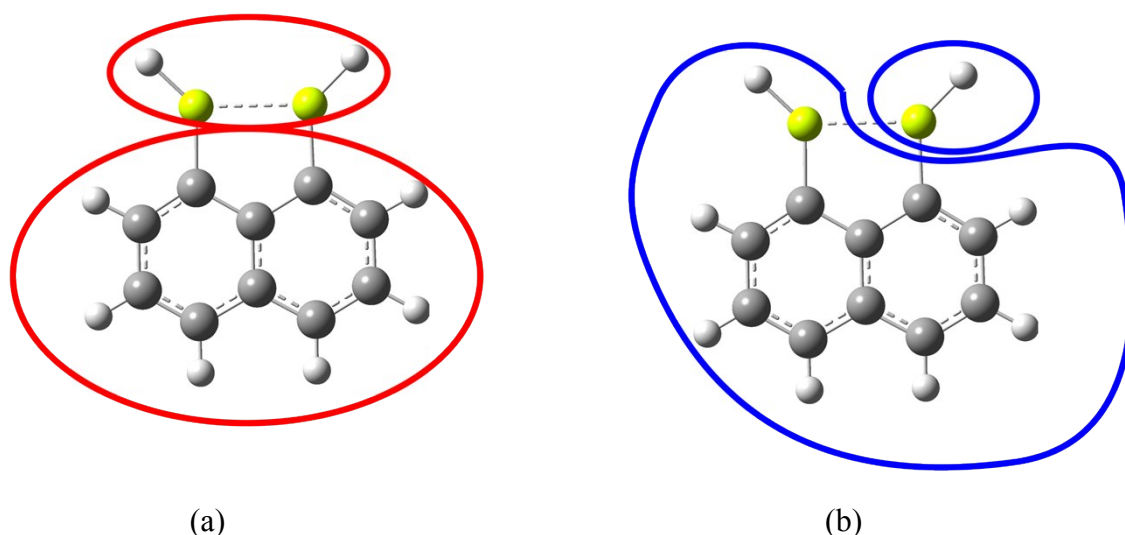
Scheme. Molecular fragmentation considered in the LMOEDA calculation for the 1,8 BeH-naphthalene anion. (a) HBeBeH + $C_{10}H_8$ and (b) BeH + $C_{10}H_8$BeH fragments.

The values of the Energy Decomposition Analysis (EDA) for the two fragmentations are given in the following Table S6.

Table S6. Energy decomposition analysis of 1,8 BeH-naphthalene anion. The fragments correspond to those proposed in the Scheme. All values are in kJ·mol^{-1}.

Fragmentation	Eelst	Epauli	Eorb	Eint
(a)	-880.4	1288.6	-1021.5	-613.3
(b)	-762.5	1764.9	-1377.4	-375.1
Be-Be	-322.3	1120.6	-866.68	-68.4

Taking into account that in fragmentation (b) we have only the interaction associated with the formation of one C–Be bond between the $C_{10}H_8$BeH and a BeH group, and that in fragmentation (a) we have the interaction between HBe–BeH and the $C_{10}H_8$

moiety, with the formation of two C–Be bonds, the difference between the energies of fragmentation (b) – ½ of the energies of fragmentation (a), give us the energies associated with the Be–Be interaction. It can be seen that this value is rather close to the one estimated using the isodesmic reactions (1) and (2). Also importantly, the EDA shows that the orbital contribution to the interaction energy is clearly dominant.

In the second approach we have calculated the $(HBeCH_3)_2$ (anion) with C_{2v} symmetry at B3LYP/6-31+G(d,p). The structure obtained present a Be-Be distance of 2.544 Å, whereas the neutral dimer dissociates spontaneously into the two monomers.
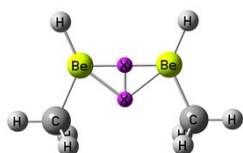

Figure S7. $(HBeCH_3)_2$ anion structure calculated at B3LYP/6-31+G(d,p) level of theory with C_{2v} symmetry.

The LMOEDA partition considering one of the monomers as neutral and the other as an anion yields the following results:

Table S7. Energy decomposition analysis for the fragmentations of the $(HBeCH_3)_2$ anion. The dimer is fragmented in a neutral and an anion monomer. All values are in $kJ \cdot mol^{-1}$.

Fragmentation	E_{elst}	E_{XC}	E_{rep}	E_{pol}	E_{DISP}	E_{int}
$HBeCH_3 + (HBeCH_3)^{-1}$	-173.8	-133.4	422.1	-182.2	-34.8	-133.4

The distortion energy of the monomers to adopt the geometry of the complex is 3.3 kJ mol^{-1} for the anion and 56.7 kJ mol^{-1} for the neutral molecule. So, the sum of the distortion energy plus the interaction energy obtained with LMOEDA amount 73.4 kJ mol^{-1}. This value is similar to the ones provided in the article for the isodesmic reactions.

[a] Peifeng Su and Hui Li, "Energy decomposition analysis of covalent bonds and intermolecular interactions" J. Chem. Phys. **2009**, 131, 014102