Bonding Analysis

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Unusually Short Be–Be Distances with and without a Bond in Be_2F_2 and in the Molecular Discuses Be_2B_8 and $Be_2B_7^-$

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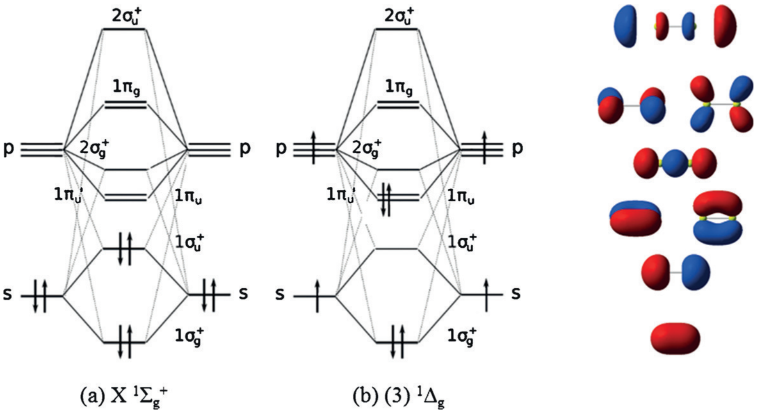
Abstract: *Quantum-chemical calculations at the CCSD(T)/cc-pVTZ level of theory show that beryllium subfluoride, Be_2F_2, has a bond dissociation energy of $D_e = 76.9\,\text{kcal mol}^{-1}$, which sets a record for the strongest Be–Be bond. The synthesis of this molecule should thus be possible in a low-temperature matrix. The discus-shaped species Be_2B_8 and $Be_2B_7^-$ possess the shortest Be–Be distance for a molecule in the electronic ground state, but there is no Be–Be bond. The cyclic species Be_2B_8 and $Be_2B_7^-$ exhibit double aromaticity with 6σ and 6π electrons, which strongly bind the Be_2 fragment to the boron atoms. The very short interatomic distance between the beryllium atoms is due to the Be–B σ and π bonds, which operate like spokes in a wheel pressing the beryllium atoms together. The formation of the Be–B bonds has effectively removed the electronic charge of the valence space between the beryllium atoms. Along the Be–Be axis, there are two cage critical points adjacent to a ring critical point at the midpoint, but there is no bond critical point and no bond path.*

Nature exhibits an enormous variety of bringing two atoms close to each other by forming a chemical bond. Classical examples are the homoatomic dimers of the first octal row, E_2 (E = Li to F), in their electronic ground states, which form single, double, or triple bonds depending on the number of valence electrons and the nature of the occupied molecular orbitals (MOs).[1] The regular increase in the formal bond order P from Li_2 ($P = 1$) to N_2 ($P = 3$),[2] which is followed by a decrease in the bond order to F_2 (P = 1), is interrupted by Be_2, which has a formal bond order of zero. The four valence electrons of Be_2 in the X $^1\Sigma_g^+$ ground state occupy the bonding $1\sigma_g^+$ and antibonding $1\sigma_u^+$ MOs (Figure 1a). This explains the rather long Be–Be distance of 2.45 Å and the small bond dissociation energy (BDE) of $D_e = 2.26 \pm 0.09\,\text{kcal mol}^{-1}$,[3,4] which most chemists will consider not to be sufficient for a genuine chemical bond.

The distinct reluctance of beryllium to form a Be–Be bond is a challenge for inventive chemists. Various ways have theoretically been probed to find species with a strong bond between two beryllium atoms. Electronically excited states of Be_2 where the electrons from the antibonding $1\sigma_u^+$ MO have been promoted to the bonding $1\pi_u$ MO are one obvious choice. High-level ab initio calculations have shown that the doubly excited singlet state $(1)^1\Delta_g[(1\sigma_u^+)^2 \rightarrow (1\pi_u^1 1\pi_u'^1)]$ has an equilibrium distance of 1.843 Å and a BDE of $D_e = 59.2\,\text{kcal mol}^{-1}$ with respect to the associated dissociation channel.[5] The corresponding triplet state of Be_2, $(1)^3\Sigma_g^-$-$[(1\sigma_u^+)^2 \rightarrow (1\pi_u^1 1\pi_u'^1)]$, has an even shorter (1.811 Å) and stronger ($D_e = 68.2\,\text{kcal mol}^{-1}$) bond. However, we were still wondering whether it would be possible to induce a strong Be–Be bond in the electronic ground state.



(a) X $^1\Sigma_g^+$ (b) (3) $^1\Delta_g$

Figure 1. Orbital correlation diagrams for a) the X $^1\Sigma_g$ ground state and b) the $(3)^1\Delta_g$ excited state of Be_2 and shape of the MOs.

Figure 2 shows the calculated[6] results for Be_2^+ and Be_2^{2+} where one or both electrons have been removed from the antibonding $1\sigma_u^+$ MO of Be_2. The bond becomes shorter in the cation (2.246 Å) and in the dication (2.130 Å) compared with neutral Be_2 (2.534 Å), which is in agreement with previous studies.[3b,7–9] The Wiberg bond order increases from 0.38 (Be_2) to 0.48 (Be_2^+) and 0.90 (Be_2^{2+}), which indicates bond strengthening. Note that the relatively high value for neutral Be_2 does not correlate with the very weak bond. The BDE of Be_2^+ ($D_e = 45.3\,\text{kcal mol}^{-1}$) signals a genuine chemical bond. The dissociation of Be_2^{2+} into atomic ions is

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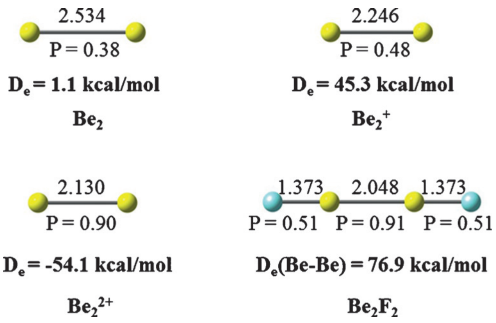

Figure 2. Bond lengths [Å] of Be_2, Be_2^+, Be_2^{2+}, and Be_2F_2 calculated at the CCSD(T)/cc-pVTZ level of theory. Wiberg bond order P determined using the CCSD/cc-pVTZ densities at the above geometries. Bond dissociation energies D_e of the Be–Be bonds at the CCSD(T)/cc-pVTZ level of theory.

exothermic by $D_e = -54.1$ kcal mol^{-1}. Previous calculations predicted that the barrier for breaking the bond is 25.5 kcal mol^{-1}, which makes the dication a metastable species.[9] To the best of our knowledge, none of the diatomic species with a strong Be–Be bond, that is, Be_2 in the electronic state, nor the cations Be_2^+ and Be_2^{2+} have been observed experimentally. The known toxicity of beryllium may be the reason for the lack of experiments. Is it possible to induce a strong Be–Be bond in the electronic ground state of a neutral molecule?

A previous study had shown that the Be–Be attraction in neutral Be_2 can be significantly enhanced by adding N-heterocyclic carbene (NHC) ligands to generate complexes of the form $(NHC^R)_n$Be–Be$(NHC^R)_n$ ($n = 1, 2$; R = H, Me, Ph; the R substituents are attached to the nitrogen atoms of the NHC).[10] The shortest Be–Be bond (1.945 Å) was calculated for (NHC^H)Be–Be(NHC^H), which has a BDE of $D_e = 39.8$ kcal mol^{-1}. A slightly longer Be–Be bond (1.978 Å) was computed for the phenyl-substituted homologue (NHC^{Ph})Be–Be(NHC^{Ph}), which has, however, a much higher BDE of $D_e = 64.7$ kcal mol^{-1}. The two systems set the record for the shortest and strongest[11] Be–Be bonds in neutral systems that were calculated thus far. Related compounds with β-dikeminate (Nac-Nac) ligands and higher-coordinated complexes $(NHC^R)_2$Be–Be$(NHC^R)_2$ feature longer and weaker Be–Be bonds.[10]

We thus searched for neutral compounds in the electronic ground state that have strong Be–Be bonds. Figure 2 shows the calculated structure of diberyllium difluoride (beryllium subfluoride, Be_2F_2). The computed Be–Be distance of 2.048 Å, which complies with the standard value for a single bond (2.04 Å),[12] is much shorter than in the diatomic systems Be_2^q ($q = 0, +1, +2$) but longer than in (NHC^R)Be–Be(NHC^R).[10] However, the BDE of Be_2F_2 ($D_e = 76.9$ kcal mol^{-1}) is larger than that of the NHC complexes. This can be explained in terms of the electronic reference state of Be_2 in (NHC^R)Be–Be(NHC^R), which is the excited $(3)^1\Delta_g$ state (Figure 1b).[10] The latter state lies 64.0 kcal mol^{-1} above the $X^1\Sigma_g^+$ ground state.[13] Thus the intrinsic interaction energies of the Be–Be bond in the complexes (NHC^R)Be–Be(NHC^R) are higher than the BDE because the antibonding $1\sigma_u^+$ MO is formally[14] vacant while the bonding $1\pi_u'$ MO is occupied (Figure 1b). It remains that Be_2F_2 has the highest Be–Be BDE that has been reported thus far. The calculated value, $D_e = 76.9$ kcal mol^{-1}, becomes $D_o^{298} = 65.0$ kcal mol^{-1} after temperature and entropy effects have been considered. The dissociation into the most stable fragments BeF_2 and Be is endergonic by $\Delta G_o^{298} = 34.2$ kcal mol^{-1}, which means that isolated Be_2F_2 is thermodynamically stable towards dissociation. The large heat of formation of the Be atom ($\Delta H_f = 77.4$ kcal mol^{-1})[15a] and the heat of sublimation of BeF_2 ($\Delta H_{sub} = 55.6$ kcal mol^{-1})[15b] render it unlikely that beryllium subfluoride can be prepared as bulk material. However, it should be possible to synthesize Be_2F_2 in a low-temperature matrix and in the gas phase. Calculations of other isomers showed that they are much higher in energy than linear Be_2F_2 (see the Supporting Information, Table S1).

The occupied MOs of Be_2F_2 provide a straightforward picture of the bonding situation (Figure 3). The HOMO correlates with the bonding $1\sigma_g^+$ of Be_2 (Figure 1) and describes the Be–Be bond. HOMO-3 and HOMO-4 represent the Be–F σ bonds. HOMO-4 is the out-of-phase combination of the B/F lobes while HOMO-3 is the in-phase combination. This means that the HOMO-3 of Be_2F_2 correlates with the Be–Be bonding orbital $2\sigma_g^+$ of Be_2 (Figure 1), which cancels the Be–Be antibonding contribution of HOMO-4. The latter orbital corresponds to the $1\sigma_u^+$ MO of Be_2. HOMO-3 and HOMO-4 have only very small coefficients in the region between the beryllium atoms. The degenerate HOMO-1 and HOMO-2 orbitals indicate significant F→Be π donation in Be_2F_2. Thus the beryllium atoms in Be_2F_2 have a filled octet shell although they are only dicoordinated. A complete MO correlation diagram for the orbital interactions between Be_2 and F_2 is shown in Figure S1. The LUMO of the molecule is the degenerate Be–Be π MO (Figure 3). It indicates that Be_2F_2 may become further

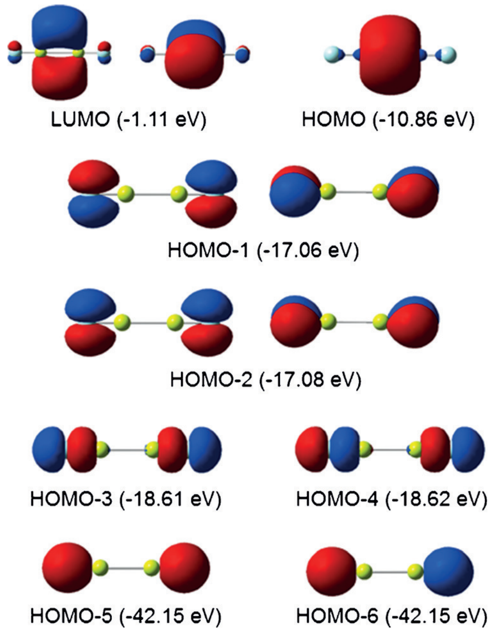

Figure 3. Shapes and eigenvalues of the lowest unoccupied MO (LUMO) and the relevant occupied valence orbitals of Be_2F_2.

stabilized by donor ligands. We are currently exploring possible structures of that type.

We found two other molecules with highly unusual Be_2 fragments. The optimized geometries of (D_{8h}) Be_2B_8 and (D_{7h}) $Be_2B_7^-$, which exhibit a discus-shaped equilibrium geometry where the Be–Be axis is perpendicular to the boron rings, are shown in Figure 4. Extensive calculations revealed that the cyclic structures are the global minima on the respective potential energy surfaces. Energetically higher-lying local minima in the singlet and triplet state are shown in the Supporting Information (Figure S2, Table S2). Molecules with boron wheels that contain more than one atom in the center, such as C_2B_8, $C_3B_9^{3+}$, and $C_5B_{11}^+$, have been found before, but the central carbon atoms in these species are all in the molecular plane.[16] The calculated Be–Be distances of 1.910 Å (Be_2B_8) and 1.901 Å ($Be_2B_7^-$) are very short. They are even shorter than in Be_2F_2, and they set a record for a short Be–Be distance in a diberyllium compound in the electronic ground state of a global-energy-minimum species. This poses questions with regard to the nature of the beryllium–beryllium interactions in Be_2B_8 and $Be_2B_7^-$.

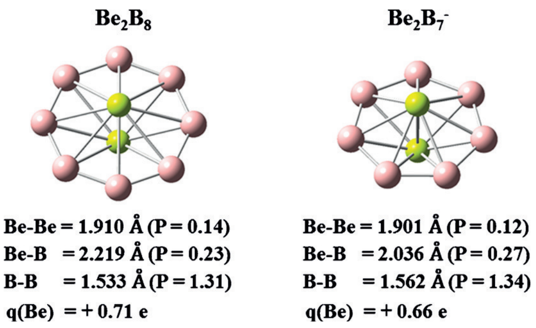

Figure 4. Calculated geometries of Be_2B_8 and $Be_2B_7^-$ at the CCSD(T)/cc-pVTZ level of theory. The theoretical bond lengths and Wiberg bond orders *P* as well as the atomic partial charge at the beryllium atom, *q*(Be), are also given. The latter values are taken from the electron densities at the CCSD/cc-pVTZ level of theory.

The Wiberg bond orders $P_{\text{Be-Be}}$ are surprisingly small (Figure 4). The values of $P = 0.14$ (Be_2B_8) and $P = 0.12$ ($Be_2B_7^-$) are even smaller than for Be_2 (0.38, Figure 2), which does not have a genuine chemical bond. In contrast, the Wiberg bond order for the Be−Be single bond in Be_2F_2 ($P = 0.91$) is much higher (Figure 2). The B−B bonds in the cyclic species, which are significantly shorter (1.533 Å in Be_2B_8 and 1.562 Å in $Be_2B_7^-$) than a standard single bond (1.70 Å),[12] have bond orders of $P = 1.31$ and $P = 1.34$, respectively. The beryllium atoms carry large positive charges of $q = +0.71$ e in Be_2B_8 and $q = +0.66$ e in $Be_2B_7^-$, which indicate strong charge donations of 1.42 e ($Be_2 \rightarrow B_8$) and 1.32 e ($Be_2 \rightarrow B_7^-$). The positive charge at beryllium in Be_2B_8 is even higher than in Be_2F_2 ($q = +0.69$ e), and the negatively charged B_7^- ring attracts nearly as much electronic charge from Be_2 as the two fluorine atoms. This indicates a remarkable charge distribution in the cyclic species.

We analyzed the electron density distribution in Be_2B_8 and $Be_2B_7^-$ with the QTAIM (quantum theory of atoms in molecules) method that was developed by Bader.[17] The Laplacian distribution $\nabla^2\rho(r)$ and the bond paths and critical points of Be_2B_8 in a plane that bisects the B_8 ring and contains two boron atoms and Be_2 are shown in Figure 5 (top) whereas Figure 5 (bottom) displays the QTAIM results for the B_8 ring. The situation in $Be_2B_7^-$ (Figure S3) is very similar. There are two areas of charge concentration ($\nabla^2\rho(r) < 0$, red dashed lines) at the beryllium atoms pointing towards the boron atoms. There are eight bond critical points (green dots) and eight ring critical points (red dots), which appear like a pearl necklace around the beryllium atoms arising from the Be–B interactions and the triangular planes that are spanned by two adjacent boron atoms and one beryllium atom. The most important information about the nature of the Be–Be interactions comes from the critical points along the interatomic axis. There is a ring critical point at the midpoint of the Be–Be distance, which belongs to the B_8 plane. At both sides of the ring critical point, there are cage critical points, which

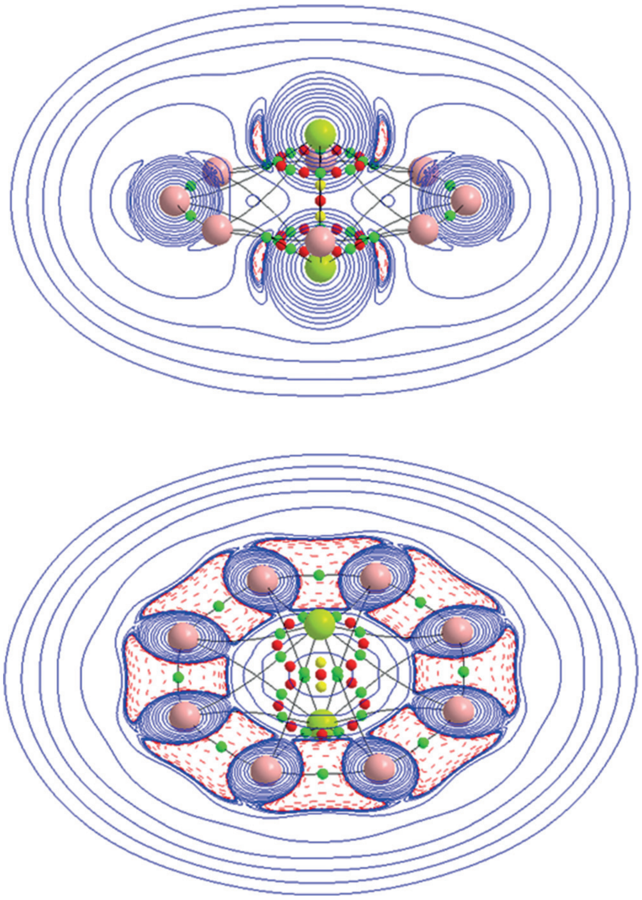

Figure 5. Plot of the Laplacian $\nabla^2\rho(r)$ and critical points and bond paths of Be_2B_8 in two different molecular planes. Top: The plane that contains the Be atoms and two opposing B atoms bisecting the plane of the B_8 ring. Bottom: The plane of the B_8 ring. Red dashed lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while solid blue lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The solid lines connecting the atomic nuclei are the bond paths. Green dots are bond critical points, red dots are ring critical points, and the two yellow dots are the cage critical points.

are at the center of the two pyramids that have an octagonal basal plane spanned by the eight boron atoms and a beryllium atom at the top. There is no bond path and no bond critical point along the Be–Be axis. The very short Be–Be distance does not come from direct chemical bonding between the beryllium atoms, but from the forces of the eight Be−B bonds, which act like spokes in a wheel and enforce a close Be−Be contact. Further bonding analyses support this remarkable electronic structure.

We inspected the molecular valence orbitals of Be_2B_8 and $Be_2B_7^-$ that are shown in the Supporting Information (Figures S4 and S5). Both molecules possess two sets of three occupied delocalized MOs that extend over the whole molecule and have σ and π symmetry, respectively. The remaining occupied MOs of Be_2B_8 and $Be_2B_7^-$ extend over the boron atoms. The bonding situation can be analyzed with the help of the AdNDP (adaptive natural density partitioning) method developed by Zubarev and Boldyrev.[18] The AdNDP method is well suited to provide a straightforward description of the bonding situation in molecules with strongly delocalized bonds.[19] Figure 6 shows the five types of orbitals that are given by the AdNDP calculations for Be_2B_8. The AdNDP orbitals for $Be_2B_7^-$ look very similar (Figure S6).

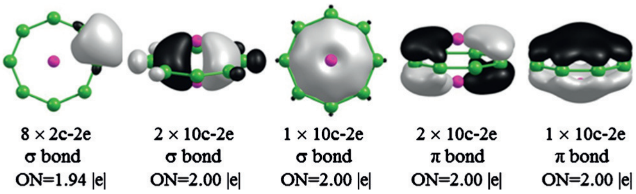

Figure 6. AdNDP analysis for Be_2B_8 computed at the PBE0/aug-cc-pVTZ level of theory. Shapes of the two-center-two-electron (2c-2e) bonds and the ten-center-two electron (10c-2e) bonds. ON is the occupation number of the MOs.

There are three delocalized σ MOs, which extend over all 10 atoms (10c-2e), one of them being degenerate. There is a similar set of three delocalized π MOs—with one degenerate one—that extend over all atoms. The six orbitals are actually nearly unchanged from the original canonical MOs, which are shown in Figures S4 and S5. The shape of the MOs clearly shows that Be_2B_8 and $Be_2B_7^-$ are doubly σ- and π-aromatic molecules. There are eight localized B−B σ orbitals (2c-2e) in Be_2B_8 (Figure 6) and seven 2c-2e MOs in $Be_2B_7^-$ (Figure S6), which describe the boron–boron bonds in the ring moieties. The only orbital that solely depicts Be−Be bonding in Be_2B_8 and $Be_2B_7^-$ is the LUMO (Figures S4 and S5).

We calculated the nuclear independent chemical shift (NICS)[23] values of Be_2B_8 and $Be_2B_7^-$ to evaluate the effect of the double aromaticity on the magnetic current. Boldyrev and Wang have reported that the double (σ + π) aromaticity in B_3^- yields a large negative value at the center of the ring, which strongly decreases at a distance of 1 Å above the center because only π aromaticity prevails.[24] The discus-shaped molecules Be_2B_8 and $Be_2B_7^-$ present particular features because there are atoms approximately 1 Å above and below the center of double aromaticity. Table 1 shows the calculated NICS values and the $NICS_{ZZ}$ component of the tensor, which have been proven to be particularly sensitive to electronic delocalization.[25] The large negative values at the center of the B_8 ring suggest a high aromatic character, which agrees with the notion of double σ and π aromaticity. The largest NICS and $NICS_{ZZ}$ values at 1.0 Å were obtained at a position close to the beryllium nuclei. $NICS_{ZZ}$ values as high as −100.3 ppm have been reported for cyclic C_3^{2+}, which was diagnosed as a doubly (σ + π) aromatic molecule.[25c]

Table 1: NICS values [ppm] of Be_2B_8 and $Be_2B_7^-$ at the center of the B_8 ring and at intervals *R* of 0.5 Å along the Be−Be axis. The data were calculated at the PBE0/aug-cc-pVTZ level of theory using the CCSD(T)/cc-pVTZ optimized structures.

	Be_2B_8 (D_{8h})		$Be_2B_7^-$ (D_{7h})	
	R [Å]	Shift [ppm]	*R* [Å]	Shift [ppm]
NICS	0.0	−34.4	0.0	−37.4
	0.5	−23.3	0.5	−26.3
	1.0	−72.2	1.0	−57.4
	1.5	−0.3	1.5	4.2
	2.0	−9.2	2.0	−8.4
	2.5	−7.2	2.5	−7.0
$NICS_{ZZ}$	0.0	−85.5	0.0	−89.5
	0.5	−87.0	0.5	−88.7
	1.0	−178.4	1.0	−174.0
	1.5	−50.2	1.5	−49.0
	2.0	−30.4	2.0	−29.6
	2.5	−19.9	2.5	−19.3

The calculations suggest that Be_2B_8 and $Be_2B_7^-$ are doubly aromatic molecules with a 6σ and 6π electron structure. There are eight (seven) further classical 2c-2e σ MOs in Be_2B_8 ($Be_2B_7^-$), which describe the B−B σ bonds. The twelve electrons of the aromatic electron structure depict the bonding between the Be_2 fragment and the boron rings and enhance the B−B bonds. There are no direct occupied Be−Be bonding orbitals as there is only indirect attraction between the beryllium atoms via the aromatic system. This explains the rather large B−B bond order and the very small value for the Be–Be interaction. The bonding picture is in agreement with the occupation of the atomic orbitals (AOs) of Be. The NBO calculations suggest a configuration of $2s^{0.33}2p_x^{0.34}2p_y^{0.34}2p_z^{0.21}$ for the beryllium atoms in Be_2B_8 and a configuration of $2s^{0.29}2p_x^{0.39}2p_y^{0.39}2p_z^{0.23}$ in $Be_2B_7^-$ where *z* is the Be−Be axis. This indicates a significantly higher occupation of the p(π) AOs of Be than the p(σ) AOs, which suggests that the electronic reference state of Be_2 is an excited state where the π orbitals are occupied. The configuration of the Be atoms agrees with the local charge concentration in the π area, which is found in the Laplacian at the Be_2 fragments in Be_2B_8 (Figure 5a) and $Be_2B_7^-$ (Figure S3a).

We calculated the bonding situation between Be_2 and the boron ring in Be_2B_8 with the energy decomposition analysis (EDA)[20] method using various electronic states and charges of the two fragments to identify the best description of the interacting species (see Table S4). The interaction between Be_2^+ in the quartet state with the electronic configuration

$1\sigma_u^{+}1\pi_u^{1}1\pi_u'^{1}$ and B_8^- in the symmetry-adapted quartet state gives the smallest value for the orbital term ΔE_{orb}, indicating the most favorable fragments.[21] The $1\sigma_u^{+}$ MO is Be–Be antibonding (Figure 1), and the degenerate $1\pi_u^{1}$ and $1\pi_u'^{1}$ MOs are used for the bonding with the B_8 ring rather than for direct Be–Be π bonding. The Be_2–B_8 interactions take place between the boron ring and two beryllium atoms that are not directly bonded to each other. Indirect Be–Be bonding is due to the σ- and π-aromatic interactions in the molecule. The electronic valence charge in the interatomic region of Be_2 has essentially been removed by the bonding with the boron atoms. In spite of the very short interatomic distances, there are no genuine Be–Be bonds in Be_2B_8 and $Be_2B_7^-$.

Aromaticity is primarily associated with energetic stabilization by cyclic delocalization. The calculated bond strength between the Be_2 moiety and the B_8 ring in Be_2B_8 suggests a very strong attraction. A previous study has shown that the global energy minimum of B_8 is a planar seven-membered ring with one boron atom in the center (D_{7h}) in the ^3A_g triplet state.[26] The BDE for Be_2B_8 yielding Be_2 and B_8 using the global energy minima calculated at the CCSD(T)/cc-pVTZ level of theory is rather high:

$$Be_2B_8(^1A_g) \rightarrow Be_2(^1\Sigma_g^{+}) + B_8(D_{7h};\ ^3A_g) \qquad (1)$$

$$D_e = 144.8\ \text{kcal mol}^{-1}$$

The intrinsic interaction energy between Be_2 and the B_8 ring is even higher. The calculated energy difference between Be_2B_8 and the fragments B_8 and Be_2 in the frozen geometries of the molecule and the quintet reference state[27] is 352.5 kcal mol^{-1}:

$$Be_2B_8(^1A_g) \rightarrow Be_2(\text{frozen, quintet}) + B_8(\text{frozen, quintet}) \qquad (2)$$

$$D_e = 352.5\ \text{kcal mol}^{-1}$$

The strong Be–B bonds yield a strong compression on the beryllium atoms. Although there are no direct Be–Be bonds in the cyclic species, the calculated Be–Be stretching modes in Be_2B_8 (854.1 cm^{-1}) and $Be_2B_7^-$ (862.9 cm^{-1}) are significantly higher than in Be_2F_2 (361.7 cm^{-1}), Be_2^+ (518.2 cm^{-1}), and Be_2^{2+} (641.9 cm^{-1}; see the Supporting Information, Table S8). It appears that the interaction of the B_8 ring with the Be_2 moiety also strengthens the B–B bonds. The boron–boron distances in Be_2B_8 (1.533 Å) are shorter than in the ring of the wheel structure (D_{7h}; ^3A_g) of B_8 (1.568 Å).

Roszak et al. have theoretically analyzed a Be_2 dimer fragment that is bonded to a carbon network and exhibits an even shorter interatomic distance than our compounds, namely close to 1.7 Å.[22] The shortest Be–Be distance of 1.718 Å was calculated for $CH_2Be_2H_2$ where a doubly bridged Be_2H_2 moiety is bonded to methylene with the Be_2 dimer orthogonal to the CH_2 plane. The authors wrote that the short Be–Be distance suggests the importance of low-lying electronic states to the bonding situation. We recalculated $CH_2Be_2H_2$ at the CCSD(T)/cc-pVTZ level of theory, which gave a Be–Be distance of 1.723 Å (Table S5). Analysis of the electronic structure reveals similar features as in our Be_2B_8 and $Be_2B_7^-$ molecules. There is no Be–Be bond path between the strongly positively charged Be atoms ($q = +0.68$), and the bond order $P = 0.40$ is close to the value for Be_2 (Figure S7, Table S4). Like in Be_2B_8 and $Be_2B_7^-$, there is no Be–Be bond in $CH_2Be_2H_2$. However, we found two other isomers, $CH_2(BH)_2$ and CH_3BeBeH, which are 39.2 and 26.2 kcal mol^{-1} lower in energy than $CH_2Be_2H_2$ (Table S5). We also found energetically lower lying isomers of the other molecules that had been reported with short Be–Be distances in the paper by Roszak et al.[22] in which Be_2H_2 fragments replaced CH in benzene. The Be_2B_8 and $Be_2B_7^-$ structures that are reported here represent the first examples where a short Be–Be distance without a bond is found in isomers that are the global energy minima.

In summary, quantum-chemical calculations have shown that beryllium subfluoride, Be_2F_2, has a bond dissociation energy of $D_e = 76.9$ kcal mol^{-1}, which sets a record for the strongest Be–Be bond. The synthesis of the molecule may thus be possible in a low-temperature matrix. The discus-shaped species Be_2B_8 and $Be_2B_7^-$ show the shortest Be–Be distances for a molecule in the electronic ground state of the global energy minimum, but there is no Be–Be bond. The cyclic compounds Be_2B_8 and $Be_2B_7^-$ exhibit double aromaticity with 6σ and 6π electrons, which bind the Be_2 fragment to the boron atoms. The very short interatomic distance between the beryllium atoms is due to the fact that the Be–B σ and π bonds operate like spokes in a wheel, pressing the beryllium atoms together. The formation of the Be–B bonds has effectively removed the electronic charge of the valence space between the beryllium atoms. Along the Be–Be axis, there are two cage critical points adjacent to a ring critical point at the midpoint, but no bond critical point and no bond path were found.

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[1] For a comparative analysis of the chemical bonds in E_2 (E = Li–F), see: A. Krapp, F. M. Bickelhaupt, G. Frenking, *Chem. Eur. J.* **2006**, *12*, 9196–9216.

[2] For a stimulating debate on the bond order in C_2, see: a) W. Zou, D. Cremer, *Chem. Eur. J.* **2016**, *22*, 4087–4099; b) M. Hermann, G. Frenking, *Chem. Eur. J.* **2016**, *22*, 4100–4108; c) M. Piris, X. Lopez, J. M. Ugalde, *Chem. Eur. J.* **2016**, *22*, 4109–4115; d) S. Shaik, D. Danovich, B. Braida, P. C. Hiberty, *Chem. Eur. J.* **2016**, *22*, 4116–4128; e) D. L. Cooper, R. Ponec, M. Kohout, *Mol.*

Phys. DOI: 10.1080/00268976.00262015.01112925, and references therein.

[3] a) V. E. Bondybey, *Chem. Phys. Lett.* **1984**, *109*, 436–441; b) J. M. Merritt, V. E. Bondybey, M. C. Heaven, *Science* **2009**, *324*, 1548–1551.

[4] For a review on experimental and theoretical studies of Be_2, see: M. C. Heaven, J. M. Merritt, V. E. Bondybey, *Annu. Rev. Phys. Chem.* **2011**, *62*, 375–393.

[5] P. J. Bruna, J. S. Wright, *Can. J. Chem.* **1996**, *74*, 998–1004.

[6] All geometry and energy calculations in this paper were carried out at the CCSD(T)/cc-pVTZ level of theory, unless otherwise stated. Additional calculations were performed at the PBE0/aug-cc-pVTZ level of theory, which agree closely with the CCSD(T) results. For a description of the theoretical methods and further references see the Supporting Information.

[7] For calculations of Be_2, see: a) A. V. Mitin, *Int. J. Quantum Chem.* **2011**, *111*, 2560–2567; b) I. Røeggen, J. Almlöf, *Int. J. Quantum Chem.* **1996**, *60*, 453–466; c) J. Stärck, W. Meyer, *Chem. Phys. Lett.* **1996**, *258*, 421–426.

[8] For calculations of Be_2^+, see: a) S. Banerjee, J. N. Byrd, R. Côté, H. H. Michels, J. A. Montgomery, Jr., *Chem. Phys. Lett.* **2010**, *496*, 208–211; b) P. J. Bruna, B. Q. Meng, J. S. Wright, *J. Mol. Spectrosc.* **1993**, *159*, 79–95.

[9] For calculations of Be_2^{2+}, see: C. W. Bauschlicher, M. Rosi, *Chem. Phys. Lett.* **1989**, *159*, 485–488.

[10] a) S. A. Couchman, N. Holzmann, G. Frenking, D. J. D. Wilson, J. L. Dutton, *Dalton Trans.* **2013**, *42*, 11375–11384; for a recent review on the coordination chemistry of beryllium, see: b) K. J. Iversen, S. A. Couchman, D. J. D. Wilson, J. L. Dutton, *Coord. Chem. Rev.* **2015**, *297–298*, 40–48.

[11] Here, we take the BDE as a measure for the bond strength of a bond A–B, which is only valid when the electronic reference states of the fragments A and B are the same as in the electronic ground state of the relaxed species A and B.

[12] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186–197.

[13] M. Pecul, M. Jaszuński, H. Larsen, P. Jørgensen, *J. Chem. Phys.* **2000**, *112*, 3671–3679.

[14] The $1\sigma_u^+$ MO of Be_2 becomes partially occupied by donation from the out-of-phase combination of the carbon lone-pair σ orbitals of the NHC ligand. The in-phase combination of the carbon lone-pair orbitals of the NHC likewise donates into the vacant $2\sigma_g^+$ MO of Be_2. For a detailed discussion of the bonding situation in $(NHC^{Ph})Be{-}Be(NHC^{Ph})$, see Ref. [10].

[15] a) W. E. Dasent, *Inorganic Energetics*, *2nd ed.*, Cambridge University Press, New York, **1982**, p. 35; b) J. Efimenko, *Nat. Bur. Stand.* **1968**, *72A*, 75–80.

[16] S. Erhardt, G. Frenking, Z. Chen, P. v. R. Schleyer, *Angew. Chem. Int. Ed.* **2005**, *44*, 1078–1082; *Angew. Chem.* **2005**, *117*, 1102–1106.

[17] R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Oxford University Press, Oxford, **1990**.

[18] D. Y. Zubarev, A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5207–5217.

[19] a) D. Y. Zubarev, A. I. Boldyrev, *J. Org. Chem.* **2008**, *73*, 9251–9258; b) D. Y. Zubarev, A. I. Boldyrev, *J. Phys. Chem. A* **2009**, *113*, 866–868.

[20] T. Ziegler, A. Rauk, *Theor. Chim. Acta* **1977**, *46*, 1–10.

[21] a) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260–3272; b) Q. Zhang, W.-L. Li, C.-Q. Xu, M. Chen, M. Zhou, J. Li, D. M. Andrada, G. Frenking, *Angew. Chem. Int. Ed.* **2015**, *54*, 11078–11083; *Angew. Chem.* **2015**, *127*, 11230–11235; c) D. M. Andrada, G. Frenking, *Angew. Chem. Int. Ed.* **2015**, *54*, 12319–12324; *Angew. Chem.* **2015**, *127*, 12494–12500.

[22] R. Roszak, S. Roszak, D. Majumdar, L. Firlej, B. Kuchta, J. Leszczynski, *J. Phys. Chem. A* **2014**, *118*, 5727–5733.

[23] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikemma Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

[24] a) A. I. Boldyrev, L. S. Wang, *Chem. Rev.* **2005**, *105*, 3716–3757; b) A. N. Alexandrova, A. I. Boldyrev, H.-J. Zhai, L.-S. Wang, *Coord. Chem. Rev.* **2006**, *250*, 2811–2866.

[25] a) C. Corminboeuf, T. Heine, G. Seifert, P. v. R. Schleyer, J. Weber, *Phys. Chem. Chem. Phys.* **2004**, *6*, 273–276; b) J. O. C. Jiménez-Halla, E. Matito, J. Robles, M. Solà, *J. Organomet. Chem.* **2006**, *691*, 4359–4366; c) A. C. Tsipis, I. G. Depastas, C. A. Tsipis, *Symmetry* **2010**, *2*, 284–319.

[26] H.-J. Zhai, A. N. Alexandrova, K. A. Birch, A. I. Boldyrev, L.-S. Wang, *Angew. Chem. Int. Ed.* **2003**, *42*, 6004–6008; *Angew. Chem.* **2003**, *115*, 6186–6190.

[27] The electronic reference state for the neutral fragments Be_2 and B_8 is suggested by the EDA results, which show that the quintet state gives the smallest ΔE_{orb} values (Table S4 a).

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