The solid state structure of Be[N(SiMe3)2]2 (1) was determined by in situ crystallisation and the bonding situation investigated by quantum chemical calculations. The Be–N bond is predominantly ionic, but some evidence for the presence of a partial Be–N double bond character was found.

Beryllium chemistry has led a cinderella-like existence compared to the heavier group 2 elements, in particular Mg, due to the toxicity of beryllium and its compounds.1 This has changed significantly in the last decade and highly interesting compounds such as beryllium diorganyls,2 NHC-stabilized beryllium dihalides,3 diorganyls,4 and hydride (i-PrNHC-Be(Me)H),5 or the Lewis acid–base adducts for monomeric aminoboranes R2BNR,6 double bond, and monomeric iminoboranes RBNR,6 their bonding situation by quantum chemical calculations. The Be–N bond is predominantly ionic, but some evidence for the presence of a partial Be–N double bond character was found.

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Theoretical computations with dispersion corrected density functional theory confirm this picture. Geometric optimizations lead to a \( S_3 \)-symmetrical structure 1a with a Be–N bond length of 1.525 Å and a perfectly planar environment of the N atoms (Si–N–Si angle 128.3°). The Si–N–N–Si torsion angle is 90°.

Geometry optimizations of Be(NR)\(_2\) (R = SiH\(_3\), Me, OH, F; Table 1) as well as of BeMe\(_2\) (C\(_2\), O–Be–O 175.3°, H–O–O–H 96.6°), and BeF\(_2\) (D\(_{2h}\)) indicate a certain double bond character, indicating the expected ionic interaction, while it is negative for 5, which in combination with the positive value of \( \Delta \rho(r_c) \) is indicative of mixed closed shell/shared interaction cases. While 6 has a nearly vanishing \( H(r_c) \), the bond critical point parameters of 1a–4 resemble more closely that of the metal organic BeMe\(_2\) 5 (cf. Table 1). Accepting the resulting picture of strongly polar covalent Be–N bonds, the bond ellipticities \( \varepsilon \) (0.07 (1a)–0.13 (4)) together with the dumbbell-shaped localization regions of the electron localization function (ELF)\(^{24} \) between the Be and N atoms (cf. Fig. 2 and Fig. S2–5, ESI\(^+\)) indicate a certain double bond character.

The solid state structure of Be[N(SiMe\(_3\))\(_2\)] 1 was determined using an \( in \) \( situ \) crystallisation approach. Quantum chemical calculations on different beryllium diamides Be(NR)\(_2\) with different steric and electronic properties prove that the Be–N bond is strongly polarized and should therefore be described as predominantly ionic. However, some evidence for the presence of a partial Be–N double bond character in 1 was also found.

We thank one of the referees for fruitful discussions and hinting on the possibility of an \( S_4 \) minimum structure of 1a.

**Table 1** Geometrical parameters, AIM partial charges, densities and local energy densities at the bond critical point \( r_c \) between Be and N of the calculated (DFT/BP+D3/def2-TZVP) structures of Be(NR)\(_2\) (R = SiMe\(_3\), SiH\(_3\), Me, OH, F; cf. Table 1) and BeMe\(_2\) (D\(_{2h}\) symmetry), Be(OMe)\(_2\) (C\(_2\), O–Be–O 175.3°, H–O–O–H 96.6°), and BeF\(_2\) (D\(_{2h}\)).

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<th>Be–N [Å]</th>
<th>R–N–R [°]</th>
<th>q(Be) [e]</th>
<th>q(N) [e]</th>
<th>( \rho(r_c) ) [au]</th>
<th>( \Delta \rho(r_c) ) [au]</th>
<th>( H(r_c) ) [au]</th>
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**Notes and references**


The text starts on page 3890 and continues on page 3891.