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**Linear dicoordinate beryllium: a ^9Be solid-state NMR study
of a discrete zero-valent s-block beryllium complex^a**

C. Leroy,¹ J. K. Schuster,^{2,3} T. Schaefer,² K. Müller-Buschbaum,² H. Braunschweig,^{2,3*} D. L.
Bryce^{1,*}

1. Department of Chemistry and Biomolecular Sciences & Centre for Catalysis Research and
Innovation
University of Ottawa
10 Marie Curie Private
Ottawa, Ontario K1N 6N5
Canada

2. Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg
Germany

3. Institute for Sustainable Chemistry & Catalysis with Boron
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg
Germany

* Authors to whom correspondence may be addressed

dbryce@uottawa.ca

h.braunschweig@uni-wuerzburg.de

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Abstract

Beryllium-9 quadrupolar coupling and chemical shift tensor data are reported for bis(1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidine-2-ylidene)beryllium ($\text{Be}(\text{CAAC})_2$). These are the first such data for beryllium in a linear dicoordinate environment. The ^9Be quadrupolar coupling constant, 2.36(0.02) MHz, is the largest recorded in the solid state to date for this isotope. The span of the beryllium chemical shift tensor, 22(2) ppm, covers about half of the known ^9Be chemical shift range, and the isotropic ^9Be chemical shift, 32.0(0.3) ppm, is the largest reported in the solid state to our knowledge. DFT calculations reproduce well the experimental data. A natural localized molecular orbital approach has been used to explain the origins and orientation of the beryllium electric field gradient tensor. The single-crystal X-ray structure of a second polymorph of $\text{Be}(\text{CAAC})_2$ is also reported. Inspection of the powder X-ray diffraction (PXRD) data shows that the new crystal structure is part of the bulk product next to another crystalline phase. Therefore, experimental X-ray powder data for the microcrystalline powder sample and the SSNMR data do not fully match either the originally reported crystal structure (Arrowsmith et al., *Nature Chem.* **2016**, 8, 890–894) or the new polymorph. The ability of solid-state NMR and PXRD to characterize powdered samples was thus particularly useful in this work.

57 Introduction

58 Beryllium is an alkaline earth metal which possesses the greatest electronegativity and
 59 smallest atomic radius of its family.¹ It can often be found in complexes with an oxidation
 60 state of +2;^{2,3} however, because of its aptitude to form strong covalent bonds, zero oxidation
 61 state compounds can also be synthesized. Recently, linear dicoordinate Be(0) compounds
 62 were reported by Arrowsmith and coworkers,⁴ thanks to stabilization by CAAC (cyclic alkyl
 63 amino carbene) ligands. Bis(1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidine-2-
 64 ylidene)beryllium ([Be(CAAC)₂]) features for the first time a covalently bonded doubly-
 65 coordinated beryllium atom which resides in a particularly linear bonding environment
 66 (Figure 1). This complex is the first of its kind, that is to say, one which features a zero
 67 oxidation state alkaline earth metal center in a closed-shell configuration. The beryllium
 68 metal center is involved in partial beryllium-carbon double-bonds (1.664(2) Å and
 69 1.659(5) Å). The linearity of the C-Be-C motif is characterized by an angle $\theta_{\text{C-Be-C}}$ of 180°
 70 (corresponding to the carbon-beryllium-carbon angle).

71 **Figure 1.** Left: schematic representation of bis(1-(2,6-diisopropylphenyl)-3,3,5,5-
 72 tetramethylpyrrolidine-2-ylidene)beryllium [Be(CAAC)₂] with Dip = 2,6-diisopropylphenyl. Middle:
 73 linear bonding geometry at beryllium, from the single-crystal X-ray crystal structure. Right:
 74 representation of the molecular geometry of the complex from the single-crystal X-ray crystal
 75 structure (Be is in light turquoise, nitrogen is in blue, carbon is in grey, hydrogen is in white).

76

77 The linear geometry and nature of the beryllium-carbon bonds in Be(CAAC)₂ can be

probed by solid-state nuclear magnetic resonance (SSNMR) via the ^9Be isotope, with significant insights from the spectra expected because of the sensitivity of the various NMR parameters to the electronic, molecular, and crystal structures. . A previous ^{11}B SSNMR study of a compound featuring linear dicoordination at boron (the dimesitylborinium cation) by Bryce et al.⁵ shows the type of information which can be obtained to understand the relation between local geometry and the different parameters extracted from SSNMR spectra. Along these lines, here we describe the nature of the local beryllium environment in $\text{Be}(\text{CAAC})_2$ through ^9Be NMR spectroscopy and density functional theory (DFT) calculations. The combination of results from both techniques should help to provide a fuller characterization of the structure about the central beryllium atom.

Beryllium-9 is a very suitable isotope for SSNMR spectroscopy as it is a quadrupolar nucleus ($I = 3/2$) with a relatively small quadrupole moment ($Q = 5.288 \times 10^{-30} \text{ m}^2$) and a natural abundance of 100 %. Its receptivity relative to ^{13}C is 81.5, and 1.39×10^{-2} relative to ^1H .⁶ Surprisingly, given the fact that ^9Be is quite amenable to SSNMR, only very few studies⁷⁻¹¹ are focused on this nuclide. This is partly explained by the very small chemical shift range of ^9Be which complicates signal differentiation, but also mainly because of the very high toxicity of many beryllium compounds. Indeed, the dust and vapor of beryllium and its compounds are dangerous to human health, as stated in previous works.¹²⁻¹⁴

As a local probe, SSNMR can reflect the coordination number and geometry about the studied nuclides thanks to the various NMR interactions. The magnitude of the nuclear electric quadrupolar interaction (QI) can be described by the quadrupolar coupling constant (C_Q) and asymmetry parameter (η_Q):

$$C_Q = \frac{eQV_{33}}{h} \quad (1)$$

$$\eta_Q = \frac{V_{11} - V_{22}}{V_{33}} \quad (2)$$

Here, V_{33} , V_{22} , and V_{11} are the principal components of the traceless electric field gradient (EFG) tensor, with $|V_{33}| \geq |V_{22}| \geq |V_{11}|$.

To describe the magnitude of the chemical shift anisotropy (CSA) arising from the magnetic shielding interaction, the Herzfeld-Berger convention is used in this work. The isotropic chemical shift (δ_{iso}), span (Ω), and skew (κ) are given as follows:

$$\delta_{\text{iso}} = \frac{(\delta_{11} + \delta_{22} + \delta_{33})}{3} \quad (3)$$

$$\Omega \approx \delta_{11} - \delta_{33} \quad (\Omega \geq 0) \quad (4)$$

$$\kappa = \frac{3(\delta_{22} - \delta_{\text{iso}})}{\Omega}; \quad (-1 \leq \kappa \leq +1) \quad (5)$$

The principal components of the chemical shift (CS) tensor are ordered as $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. The first evidence for anisotropic beryllium shielding was measured at Dalhousie University by Bryce and Wasylishen in 1999.¹¹

Generally, as the symmetry drops about a particular nucleus in a given molecule, an increase in the quadrupolar coupling constant is expected. Logically, a linear geometry presents a fairly low symmetry (with two independent directions) compared to tetrahedral or octahedral geometries. For a perfectly axially symmetric linear environment (C_n symmetry, $n > 2$), the value of η_Q must be equal to zero (or sometimes 1 as discussed in reference 15) and the value of κ is ± 1 . At the same time, the influence of the neighbouring atoms (bonded or

non-bonded) is also strongly reflected in the NMR parameters as they also influence the local electronic environment.

The purpose of this study is to provide further insight into the nature of the C-Be-C motif present at the heart of Be(CAAC)₂. Solid-state ⁹Be NMR experiments are performed in order to determine and interpret the complete beryllium quadrupolar and chemical shift tensors. These tensors are also calculated using DFT and interpreted using natural localized molecular orbital (NLMO) analyses.

Experimental

Sample preparation

CAUTION! Beryllium compounds are extremely toxic and should be handled with suitable care. Be(CAAC)₂ used for this study was prepared according to the literature procedure.⁴ Crystalline material was afforded from several crystallization cycles from a saturated Et₂O solution.

X-ray diffraction

Diffraction data for a single crystal of Be(CAAC)₂ from a saturated Et₂O solution were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated MoK_α radiation. The structure was solved using the intrinsic phasing method,¹⁶ refined with the SHELXL program,¹⁷ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystal data for $\text{Be}(\text{CAAC})_2$: $\text{C}_{40}\text{H}_{62}\text{BeN}_2$, $M_r = 579.92$, purple plate, $0.156 \times 0.057 \times 0.048 \text{ mm}^3$, Triclinic space group $P \bar{1}$, $a = 9.3383(4) \text{ \AA}$, $b = 11.8910(6) \text{ \AA}$, $c = 16.8150(8) \text{ \AA}$, $\alpha = 81.881(2)^\circ$, $\beta = 82.306(2)^\circ$, $\gamma = 78.281(2)^\circ$, $V = 1799.23(15) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.070 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.060 \text{ mm}^{-1}$, $F(000) = 640$, $T = 100(2) \text{ K}$, $R_I = 0.0539$, $wR^2 = 0.1084$, 7295 independent reflections [$2\theta \leq 52.742^\circ$] and 407 parameters (CCDC 1583864).

Samples for powder X-ray diffraction were prepared in open-stage sample holders with a poly(methylmethacrylate) (PMMA) cupola and a Si-wafer platform. The diffraction data were collected with a Bruker AXS D8 Discover powder X-ray diffractometer equipped with Lynx-Eye detector in reflection geometry. For focusing the X-ray radiation ($\text{Cu-K}\alpha 1$; $\lambda = 154.06 \text{ pm}$), a Goebel mirror was used, and $\text{Cu-K}\alpha 2$ radiation was eliminated by the application of a Ni absorber. The diffraction patterns were recorded and analyzed with the Bruker AXS Diffrac-Suite.

Solid-state NMR spectroscopy

Home-made acrylic vessel inserts for 7 mm outer diameter magic-angle spinning (MAS) rotors were used. Microcrystalline $\text{Be}(\text{CAAC})_2$ was sealed in the insert then packed into a 7 mm outer diameter ZrO_2 rotor with an O-ring cap in a glovebox under inert atmosphere (Ar). A microcrystalline powder was used without any additional grinding due to the sensitivity of the compound. There are therefore likely preferentially oriented crystallites inside the rotor which will introduce distortions or spikes in the spectra.

Data were acquired at the University of Ottawa using a Bruker AVANCE III spectrometer at a magnetic field strength of 9.4 T ($\nu_L(^9\text{Be}) = 56.25 \text{ MHz}$) and at the National

160 Ultrahigh-field NMR Facility for Solids in Ottawa using a Bruker AVANCE II spectrometer
161 which operates at a magnetic field strength of 21.1 T ($\nu_L(^9\text{Be}) = 126.42$ MHz).

162 ^9Be NMR experiments were conducted at room temperature and chemical shifts were
163 referenced externally using an aqueous 1.0 M solution of BeSO_4
164 ($\delta_{\text{iso}}(\text{Be}(\text{H}_2\text{O})_4^{2+}) = 0.0$ ppm).¹¹ Only static experiments were conducted because of safety
165 concerns associated with potential MAS rotor crashes. WURST-QCPMG¹⁸ and quadrupolar
166 echo (*i.e.*, $\pi/2$ - τ_1 - $\pi/2$ - τ_2 -acquire) experiments were used at $B_0 = 9.4$ T whereas QCPMG and
167 quadrupolar echo experiments were used on the 21.1 T spectrometer. ^1H decoupling
168 (continuous wave, CW) was used for all experiments. An optimal recycle delay of 20 s at
169 21.1 T (and 4 s at 9.4 T) was used with a central transition-optimized $\pi/2$ pulse length of 4 μs
170 on both spectrometers. Unfortunately, ^{13}C and ^1H NMR spectra were not successfully
171 recorded because of undesired dominant signals arising from the acrylic insert. Spectra were
172 simulated using WSolids software in order to extract NMR parameters from the experimental
173 ^9Be line shapes.¹⁹ Uncertainties in the reported parameters were determined via an iterative
174 heuristic approach whereby individual parameters were varied from their optimum values
175 until the simulated spectrum was clearly different from the experimental one.

176 *Computational details*

177 Calculations of the EFG and magnetic shielding tensor parameters were performed
178 using the Amsterdam Density Functional program (ADF, version 2016).^{20–22} The input
179 structure was generated from the atomic coordinates of the published crystal structure (CCDC
180 number 1439667). A geometry optimization was also conducted using the PBE functional
181 with the QZ4P basis set. Calculations were executed using various functionals and basis sets
182 (see Supporting Information). The NLMO and NBO analyses of the EFG tensors were
183 performed using the NBO program (ver. 6.0) that is incorporated into the ADF suite.

Calculations give the absolute magnetic shielding value, σ_{calc} , which is then converted into the chemical shift (δ_{calc}) according to: $\delta_{\text{calc}} \approx \sigma_{\text{ref}} - \sigma_{\text{calc}}$, where σ_{ref} is determined from calculations. Bryce et al. calculated a value of 114.96 ppm (RHF/6-311++G(3df,3pd))¹¹ and more recently Plieger and coworkers obtained $\sigma_{\text{ref}} = 108.96$ ppm (B3LYP/6-311G+(2d,p)).²³ The latter reference value yields better agreement with experiment in the current work, and has been used to compare our experimental data with predicted ones.

For plots showing $\theta_{\text{C-Be-C}}$ vs. CSA or QI parameters, structures were modified by manually changing the C-Be-C angle with GaussView 4.1 software (from the initial optimized value of 179.92° down to 159.92°), without further optimization.

Results and discussion

Figure 2. ^9Be solid-state NMR spectra of $\text{Be}(\text{CAAC})_2$ obtained using a spin echo (black). Left: static spectrum recorded at 21.1 T with 1920 transients. Right: static spectrum recorded at 9.4 T with 16912 transients. An impurity phase is shown in green. Simulated spectra based on the parameters shown in Table 1 are given in red (the blue line shape represents the signal of interest). The asterisk indicates a preferential orientation of crystallites due to the lack of thorough grinding.

The ^9Be SSNMR spectra of $\text{Be}(\text{CAAC})_2$ at two different magnetic fields are shown in Figure 2. Despite the high natural abundance of the beryllium-9 isotope, the signal-to-noise

ratio of the central transition spectra is moderate, and no satellite transitions are observed. The static spectrum is composed of two different signals which are easily distinguished: the broader second-order quadrupole-dominated line shape (in blue, total breadth ~ 13.4 kHz and ~ 24.2 kHz at 21.1 T and 9.4 T, respectively), and one rather narrow Gaussian-Lorentzian peak ($\Delta\nu_{1/2} \sim 2500$ Hz at 21.1 T, in green in Figure 2). Previously reported X-ray crystallographic data⁴ show only one distinct site for beryllium, which suggests that the Gaussian-Lorentzian component of the spectrum could be attributed to an impurity or sample deterioration, as the studied sample is highly sensitive to both moisture and oxygen. To further explore the origins of this peak, a relaxation-filtered experiment with a long echo delay ($\tau = 2025$ μ s) is presented in Figure 3. The Gaussian-Lorentzian signal is suppressed, meaning that the spin-lattice relaxation time constant (T_2) of this signal is much shorter than that for the quadrupolar line shape, further indicating that the signals arise from different components in the sample. This can be related to the crystallinity of the compounds, with the longer T_2 attributed to the more crystalline sample (as opposed to a short T_2 which may often be attributed to a more disordered material).^{24,25} During this experiment, the signal with the shorter T_2 decays when using a very long echo time whereas the more crystalline sample will still display a strong FID at the end of the echo delay. This observation would be consistent with a less crystallized or disordered phase which is not observed in powder X-ray diffractograms and would represent another beryllium phase distinct from Be(CAAC)₂ (which is known to be crystalline from the X-ray diffractogram shown in the Supporting Information, Figure S3). The powder diffractogram shows that the polymorph studied via SSNMR does not match the originally reported single-crystal structure, which can plausibly be explained by the two different crystallization conditions used for precipitating the samples.⁴ Therefore, a single crystal was selected from the new batch of the sample and a new single-crystal

structure was obtained and is reported here (CCDC 1583864). The local geometry at Be is essentially identical in both X-ray structures. Compared to the simulated powder pattern of the new single-crystal structure, the recorded diffractogram shows the reflections of the desired new crystalline structure (for example at $2\Theta = 8.8^\circ$, 10.6° , 11.2° , 11.6° , 15.3° and 19.7°) as well as additional reflections (see Supporting Information, Fig. S3). This provides clear evidence that the new polymorph of $\text{Be}(\text{CAAC})_2$ is part of the bulk product but that there is also at least one additional crystalline phase in the bulk material. Thus, the microcrystalline powder studied via SSNMR is influenced by this unknown second Be-species which explains the Gaussian-Lorentzian peak in the ^9Be SSNMR spectra.

Figure 3. Left: Static 21.1 T ^9Be quadrupolar echo spectra with $\tau = 2025 \mu\text{s}$ (1792 transients) and $25 \mu\text{s}$ respectively at the bottom and top. On the right: Simulated spectra with QI and CSA parameters based on the parameters given in Table 1. Only the parameter indicated on each spectrum is modified.

The experimental signal for $\text{Be}(\text{CAAC})_2$ cannot be properly simulated by taking only into account the QI; significant CSA needs to be added in order to obtain a proper fit at both

applied magnetic fields, as can be seen on the right in Figure 3. The spectrum recorded at 21.1 T allows for easier deconvolution of the effects of the two interactions since the signal-to-noise ratio is much better and also because the second-order QI is inversely proportional to the magnetic field, thus reducing its effect on the line shape (whereas the CSA is proportional to B_0 in Hz).

Table 1. Experimental ^9Be Quadrupolar and Chemical Shift Tensors for $\text{Be}(\text{CAAC})_2$

δ_{iso} / ppm	C_Q / MHz	η_Q	Ω / ppm	κ	α / deg	β / deg	γ / deg
32.0(0.3)	2.36(0.02)	0.88(0.02)	22(2)	-0.5(0.1)	90(5)	30(5)	275(7)

The measured experimental values (Table 1) for C_Q and η_Q are 2.36 MHz and 0.88, respectively. To our knowledge, this C_Q value is the largest recorded using SSNMR for ^9Be ; the previous values found in the literature do not exceed 1.5 MHz.¹⁰ The experimental quadrupolar and chemical shift tensor parameters will now be discussed in detail in the context of the molecular structure as well as with respect to DFT calculations and previously reported ^9Be NMR data for other compounds. Table 2 shows the results of the DFT calculations performed on $\text{Be}(\text{CAAC})_2$ with different basis sets and functionals. Additional computational results may be found in the Supporting Information (Table S2).

Table 2. Calculated ^9Be quadrupolar and magnetic shielding tensors parameters for $\text{Be}(\text{CAAC})_2$

	B3LYP ^a		BP86 ^a		B3LYP ^b
	TZ2P	QZ4P	TZ2P	QZ4P	TZ2P
C_Q / MHz	2.67	2.63	2.62	2.67	2.59
η_Q	0.88	0.80	0.94	0.86	0.91
σ_{iso} / ppm	73.4	73.7	76.0	71.6	75.8
Ω / ppm	19.3	21.0	21.6	22.2	25.1

κ	−0.31	−0.06	−0.63	−0.56	−0.27
α / deg	93	86	97	95	95
β / deg	21	13	31	24	38
γ / deg	287	298	278	281	277

^aCalculated from a geometry-optimized structure (PBE/QZ4P) on a single molecule with ADF.

^bCalculated from the available crystal structure coordinates (CCDC 1439667) on a single molecule with ADF.

Beryllium chemical shift tensors.

As stated at the beginning of this work, the isotropic CS range for ^9Be is about 50 ppm,²³ which is small relative to most other nuclides besides ^1H . Most previous ^9Be NMR reports of isotropic chemical shifts focus on solution NMR,^{23,26} although some data are available from solid-state spectroscopic studies^{8–11,27} (*vide infra*). Niemeyer and Power²⁸ observed in 1997 that lowering the coordination number of the beryllium complex results in an increased chemical shift (four-coordinated species are in the range of 2.5–5.5 ppm while three-coordinated ones are around 11–17.5 ppm). At that time, the only two-coordinated species for which a chemical shift was recorded was 15.6 ppm for $\text{ArBeN}(\text{SiMe}_3)_2$; however, this value could be explained by the probable dissociation of the complex in solution. The chemical shift range of the tetrahedral species was confirmed by Dann and Weller in the same year²⁷ with the study of different sodalite framework structures containing beryllium and featuring a CS range of −0.8 to 1.2 ppm. The experimental $\delta_{\text{iso}}(^9\text{Be})$ value measured for $\text{Be}(\text{CAAC})_2$ is 32 ppm (Table 1). This value is in the range of δ_{iso} calculated for several two-coordinate compounds (see Table 3) and more specifically in excellent agreement with the value calculated for $\text{Be}(\text{CAAC})_2$ itself ($\delta_{\text{calc}} = 32.9$ ppm). To our knowledge, it also corresponds to the most deshielded value ever observed in a ^9Be SSNMR spectrum.

The centre-of-gravity of the impurity peak (Figure 2) is at 1.8 ppm. This signal falls in the range of 4-coordinated species with high symmetry because of the Gaussian-Lorentzian

shape observed (and thus small C_Q). It could correspond to a hydrate of beryllium or a tetracoordinated species according to Plieger and coworkers.²³ Sen and Yu also show similarly shaped-spectra for Be-compounds corresponding to beryllium trapped in silicate-glass (BeO-SiO₂) with chemical shifts varying from -1.33 to 0.66 ppm. In related work, Bryce and coworkers¹¹ studied Be(acac)₂, and showed that two distinct crystallographic sites shared the same δ_{iso} of 0.22 ppm, whereas Hung et al.⁹ found δ_{iso} between -19.8 and -24.4 ppm for homoleptic beryllocenes.

Experimental span and skew parameters for Be(CAAC)₂ are 22 ppm and -0.5, respectively. This span covers nearly half of the known chemical shift range for ⁹Be. For a perfectly axially symmetric environment, a skew of ± 1 is expected. DFT predicts, for Be(CAAC)₂, quite different values depending of the level of theory (see Table 2 and S2), but in any case none of them is close to unity, meaning that the Be CS tensor is not axially symmetric. For comparison, presented in Table 3 are calculated κ values for a set of related compounds featuring side groups with much less steric bulk. Inspection of these data shows that the steric bulk of the CAAC ligand is responsible for the perhaps unexpected skew value.

Table 3. DFT calculations (BP86/TZ2P) results for two-coordinate beryllium model systems (BeR₂) and Be(CAAC)₂. All structures were optimized with ADF (PBE/QZ4P).

Side Group (R)	$ C_Q $ / MHz	η_Q	σ_{iso} / ppm	Ω / ppm	κ	θ_{C-Be-C} / deg
H	3.72	0.00	80.3	103.6	1.00	180.0
Methyl	3.72	0.00	75.4	123.4	1.00	179.7
Phenyl	3.69	0.14	83.1	90.0	0.77	179.8
Cl	2.11	0.00	94.1	110.7	1.00	179.0
CAAC	2.62	0.94	76.0	21.6	-0.63	179.9

It is well known that an axially symmetric tensor is only expected if the symmetry is rigorously C_n ($n > 2$), for example. While the coordination at beryllium in the present work is

essentially perfectly linear, the point group at beryllium does not require axial symmetry of the NMR tensors. This is due to the ligands as mentioned above. In this sense, the experimental and computed data are not out of the ordinary. Indeed, an inspection of the data in Table 3 shows that axial symmetry is only present when the proper point group symmetry is satisfied in the various model systems (i.e., in the cases of BeH_2 , $\text{Be}(\text{CH}_3)_2$, and BeCl_2).

⁹Be quadrupolar coupling constants

Again, we report the largest experimental ⁹Be quadrupolar coupling constant, $C_Q = 2.36$ MHz. The calculated C_Q values are somewhat larger than the experimental one (Table 1 and Table 3). Different levels of theory and functionals have been used on a re-optimized structure, and additional results can be found in Table 2 and in the Supporting Information. Hung *et al.*⁹ noted the transformation of a ⁹Be quadrupolar signal to a Lorentzian line shape by variable temperature experiments on several homoleptic beryllocenes (Cp_2Be , Cp_2Be^* and $(\text{C}_5\text{Me}_4\text{H})_2\text{Be}$) in concordance with a small isotropic shift. The maximum quadrupolar coupling constant they measured was $C_Q = 0.61$ MHz. One can easily notice a drastic change of C_Q expressed by the narrowing of the line width. The exact reason for this is not fully explained in their work; however, as pointed out, at higher temperature, the C_Q will be lower because of the dominance of intramolecular motions averaging the EFG tensors. It is worth mentioning that authors also observed an increase of C_Q when the spherical symmetry decreases. Keeping that in mind and returning briefly to solution studies, the work of Kanakubo and coworkers²⁹ in 1998 shows an opposite trend, that is to say the low dependency of C_Q with respect to temperature for $\text{Be}(\text{acac})_2$ in *d*-acetonitrile. Tarasov and coworkers published a study focused on the EFG in beryllium hydride, calculating $C_Q = 180$ and 135 kHz for both sites.³⁰ They also show that the ⁹Be EFG tensors

are very sensitive to the distance to nearby atoms.

The EFG asymmetry parameter & linear angle dependence

Geometry-optimized structures of the compounds in Table 3 exhibit a quasi-perfect linear structure at Be, as does Be(CAAC)₂. Although the predicted η_Q value is close to 0, which indicates an axial symmetry, for BeH₂, BeCl₂, BeMe₂ and BePh₂ (see Table 3), the calculated and experimental asymmetry parameter η_Q for Be(CAAC)₂ is 0.8 to 0.9. Both values (0 and ~1) actually describe a so called-axial symmetry; however, the difference lies in the relative magnitudes of the tensor components (and more specifically in V_{33}). In the first case ($\eta_Q = 0$), the largest EFG tensor component lies in along the axial symmetry axis whereas when $\eta_Q = 1$, this is not the case, and $|V_{22}| \approx |V_{33}|$ rather than $V_{11} \approx V_{22}$.¹⁵ We studied here the dependence on geometry of the different NMR parameters (C_Q , η_Q , Ω , and κ) by varying the $\theta_{\text{C-Be-C}}$ angle from 180° to 160° (Figure 4). These calculations show the sensitivity of these parameters to the local geometry.

Figure 4. Plots of calculated (B3LYP/TZ2P) parameters η_Q (a), C_Q (b), κ (c) and Ω (d) versus the angle θ_{C-Be-C} . Fitted trend lines are given as follows: $\eta_Q = (-7.00 \times 10^{-5})(\theta^2) + (2.47 \times 10^{-2})(\theta) - 1.35 \times 10^0$, $R^2 = 0.999$; $C_Q = (-6.00 \times 10^{-5})(\theta^2) + (2.26 \times 10^{-2})(\theta) + 6.40 \times 10^{-1}$, $R^2 = 0.999$; $\Omega = (2.30 \times 10^{-3})(\theta^2) - (8.42 \times 10^{-1})(\theta) + 9.47 \times 10^1$, $R^2 = 0.991$; $\kappa = (7.00 \times 10^{-4})(\theta^2) - (2.37 \times 10^{-1})(\theta) + 2.10 \times 10^1$, $R^2 = 0.997$.

The values of η_Q and C_Q are only slightly sensitive to this angle as they vary from 0.88 to 0.85 and 2.67 to 2.64 MHz, respectively, over the angular range. The values of Ω and κ change from 19.2 to 20.2 ppm and -0.35 to -0.05 , respectively (and σ_{iso} from 73.43 to 73.10 ppm), also showing a modest but clear dependence on angle alone.

Figure 5. Orientation of the ^9Be EFG tensor for $\text{Be}(\text{CAAC})_2$. Left: the NLMO shown is one of two symmetry-equivalent Be-C bonding orbitals. Right: V_{11} lies along the C-Be-C axis while V_{22} and V_{33} lie in the plane perpendicular to this axis.

To further explore the large difference in the values of η_Q noted in Table 3 for seemingly similar compounds, the molecular orbitals responsible for the various principal components of the EFG tensors were examined (see Figure 5). The magnitudes of V_{22} and V_{33} are very similar whereas V_{11} is an order of magnitude smaller, causing the asymmetry parameter η_Q to be 0.88 (See Supporting Information). Interestingly, calculations on a similar beryllium compound featuring linear geometry at Be, beryllium bis(diazaborolyl)³¹, gives a η_Q of 0.08 (see Supporting Information). Here, V_{33} lies along the B-Be-B axis. NLMO³² calculations on $\text{Be}(\text{CAAC})_2$ show that the two carbon-beryllium bonding orbitals make the largest contributions to V_{33} (Figure 5) and thus drive its magnitude and direction. The C-Be bonding orbitals represent the largest contributions to the three principal components of the EFG tensor (Table 4).

368 **Table 4.** NLMO Analysis of Beryllium EFG Tensors for Be(CAAC)₂ (a.u.)

	V_{22}	V_{11}	V_{33}
Be-X bonding X = C or B	-0.594	0.292	0.302
Be core	0.033	-0.016	-0.016
X core	-0.242	0.118	0.122
X LP	NA	NA	NA
All other core	-0.01	-0.062	NA
All other printed contributions	-0.007	-0.343	0.137
Total calculated	-0.193	-0.011	0.205

369

370 **Conclusions**

371 Solid-state ⁹Be NMR spectroscopy has been used to study a discrete zero-valent s-
 372 block beryllium complex. Beryllium-9 quadrupolar coupling and chemical shift tensor data
 373 have been reported for Be(CAAC)₂, the first such data for beryllium in a linear dicoordinate
 374 environment. The ⁹Be quadrupolar coupling constant is the largest recorded in the solid state
 375 to date. Despite the locally linear C-Be-C environment, the quadrupolar asymmetry
 376 parameter is far from zero as a result of the influence of the CAAC ligands. The span of the
 377 beryllium chemical shift tensor covers about half of the known ⁹Be chemical shift range, and
 378 the isotropic ⁹Be chemical shift is the largest reported in the solid state, to our knowledge.
 379 DFT calculations reproduce well the experimental data. An NLMO approach has been used
 380 to explain the origins and orientation of the beryllium EFG tensor.

381 The single-crystal X-ray structure of a second polymorph of Be(CAAC)₂ has been
 382 reported. Interestingly, X-ray powder diffractogram of the microcrystalline powder sample
 383 analyzed via SSNMR spectroscopy does not match either the originally reported crystal
 384 structure or the new polymorph. The ability of SSNMR spectroscopy and PXRD to
 385 characterize powdered samples was thus particularly useful in this work. This contribution
 386 has expanded on the limited knowledge in the literature on discrete dicoordinate beryllium

compounds and their NMR response.

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Supporting Information Available

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1583864. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Additional DFT calculations; ^9Be QCPMG spectrum; powder X-ray diffraction data.

References

- (1) Riebling, E. F.; Duke, D. A. *J. Mater. Sci.* **1967**, 2 (1), 33–39.
- (2) Mederos, A.; Domínguez, S.; Chinea, E.; Brito, F.; Cecconi, F. *J. Coord. Chem.* **2001**, 53 (3), 191–222.
- (3) Green, S. P.; Jones, C.; Stasch, A. *Science* **2007**, 318 (5857), 1754–1757.

- 410 (4) Arrowsmith, M.; Braunschweig, H.; Celik, M. A.; Dellermann, T.; Dewhurst, R. D.;
411 Ewing, W. C.; Hammond, K.; Kramer, T.; Krummenacher, I.; Mies, J.; Radacki, K.;
412 Schuster, J. K. *Nat. Chem.* **2016**, 8 (9), 890–894.
- 413 (5) Alain, A. E.; Shoji, Y.; Fukushima, T.; Bryce, D. L. *Inorg. Chem.* **2015**, 54 (24),
414 11889–11896.
- 415 (6) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P.
416 *Pure Appl. Chem.* **2001**, 73 (11), 1795–1818.
- 417 (7) Grew, E. S. *Rev. Mineral. Geochemistry* **2002**, 50 (1), 1–76.
- 418 (8) Skibsted, J.; Norby, P.; Bildsøe, H.; Jakobsen, H. J. *Solid State Nucl. Magn. Reson.*
419 **1995**, 5 (3), 239–255.
- 420 (9) Hung, I.; Macdonald, C. L. B.; Schurko, R. W. *Chem. - A Eur. J.* **2004**, 10 (23), 5923–
421 5935.
- 422 (10) Sen, S.; Yu, P. *Phys. Rev. B* **2005**, 72 (13), 132203.
- 423 (11) Bryce, D. L.; Wasylishen, R. E. *J. Phys. Chem. A* **1999**, 103 (36), 7364–7372.
- 424 (12) Maier, L. A. *J. Thorac. Imaging* **2002**, 17 (4), 273–284.
- 425 (13) Buzea, C.; Pacheco, I. I.; Robbie, K. *Biointerphases* **2007**, 2 (4), MR17-MR71.
- 426 (14) Wong, C. Y.; Woollins, J. D. *Coord. Chem. Rev.* **1994**, 130 (1–2), 243–273.
- 427 (15) Autschbach, J.; Zheng, S.; Schurko, R. W. *Concepts Magn. Reson. Part A* **2010**, 36A
428 (2), 84–126.
- 429 (16) Sheldrick, G. M. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, 71 (1), 3–8.
- 430 (17) Sheldrick, G. M. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, 64 (1), 112–122.
- 431 (18) O'Dell, L. A.; Schurko, R. W. *Chem. Phys. Lett.* **2008**, 464 (1–3), 97–102.
- 432 (19) K.Eichele. WSolids NMR Simulation Package version 1.21.3, **2015**.
- 433 (20) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen,
434 S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, 22 (9), 931–967.
- 435 (21) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.*
436 **1998**, 99 (6), 391–403.

- 437 (22) ADF2017, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The
438 Netherlands, <https://www.scm.com>. Baerends, E. J.; Ziegler, T.; Atkins, A. J.;
439 Autschbach, J.; Bashford, D.; Baseggio, O.; Bérces, A.; Bickelhaupt, F. M.; Bo, C.;
440 Boerritger, P. M.; Cavallo, L.; Daul, C.; Chong, D. P.; Chulhai, D. V.; Deng, L.;
441 Dickson, R. M.; Dieterich, J. M.; Ellis, D. E.; van Faassen, M.; Ghysels, A.;
442 Giammona, A.; van Gisbergen, S. J. A.; Goez, A.; Götz, A. W.; Gusarov, S.; Harris, F.
443 E.; van den Hoek, P.; Hu, Z.; Jacob, C. R.; Jacobsen, H.; Jensen, L.; Joubert, L.;
444 Kaminski, J. W.; van Kessel, G.; König, C.; Kootstra, F.; Kovalenko, A.; Krykunov,
445 M.; van Lenthe, E.; McCormack, D. A.; Michalak, A.; Mitoraj, M.; Morton, S. M.;
446 Neugebauer, J.; Nicu, V. P.; Noodleman, L.; Osinga, V. P.; Patchkovskii, S.;
447 Pavanello, M.; Peeples, C. A.; Philipsen, P. H. T.; Post, D.; Pye, C. C.;
448 Ramanantoanina, H.; Ramos, P.; Ravenek, W.; Rodríguez, J. I.; Ros, P.; Rüger, R.;
449 Schipper, P. R. T.; Schlüns, D.; van Schoot, H.; Schreckenbach, G.; Seldenthuis, J. S.;
450 Seth, M.; Snijders, J. G.; Solà, M.; M., S.; Swart, M.; Swerhone, D.; te Velde, G.;
451 Tognetti, V.; Vernooijs, P.; Versluis, L.; Visscher, L.; Visser, O.; Wang, F.;
452 Wesolowski, T. A.; van Wezenbeek, E. M.; Wiesenekker, G.; Wolff, S. K.; Woo, T.
453 K.; Yakovlev, A. L. .
- 454 (23) Plieger, P. G.; John, K. D.; Keizer, T. S.; McCleskey, T. M.; Burrell, A. K.; Martin, R.
455 *L. J. Am. Chem. Soc.* **2004**, *126* (44), 14651–14658.
- 456 (24) Fyfe, C. A.; Lyerla, J. R.; Volksen, W.; Yannoni, C. S. *Macromolecules* **1979**, *12* (4),
457 757–761.
- 458 (25) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979**, *12* (4), 762–767.
- 459 (26) Gaines, D. F.; Coleson, K. M.; Hillenbrand, D. F. *J. Magn. Reson.* **1981**, *44* (1), 84–88.
- 460 (27) Dann, S. E.; Weller, M. T. *Solid State Nucl. Magn. Reson.* **1997**, *10* (1–2), 89–94.
- 461 (28) Niemeyer, M.; Power, P. P. *Inorg. Chem.* **1997**, *36* (21), 4688–4696.
- 462 (29) Kanakubo, M.; Ikeuchi, H.; Satô, G. P. *J. Chem. Soc. Faraday Trans.* **1998**, *94* (21),
463 3237–3240.
- 464 (30) Tarasov, V. P.; Muravlev, Y. B.; Izotov, D. E. *Dokl. Phys. Chem.* **2005**, *404* (1–3),
465 190–194.
- 466 (31) Arnold, T.; Braunschweig, H.; Ewing, W. C.; Kramer, T.; Mies, J.; Schuster, J. K.

- 467 *Chem. Commun.* **2015**, 51 (4), 737–740.
- 468 (32) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, 83 (4), 1736–1740.
- 469

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