Supporting Information to: The Molecular Structure of Diethylaminoalane in the Solid-State: An X-ray Powder Diffraction, DFT Calculation and Raman Spectroscopy Study

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1. Comparison with DUSNAI00

Table S1 shows the lattice parameters of diethylaminoalane as deposited in the CSD by Rheingold & Hampden-Smith (2015) in comparison with the lattice parameters determined in this study at 193 K.

Table S1. *Comparison of the lattice parameters of diethylaminoalane from this study at 193 K with the lattice parameters from the structure determination by (Rheingold & Hampden-Smith, 2015).*

	a / Å	b / Å	c / Å	β / °	V / Å^3
This study	7.3547(4)	12.8953(6)	7.2174(4)	89.797(5)	684.50(5)
By Rheingold & Hampden-Smith (2015)	7.3814(6)	12.8597(11)	7.2412(6)	90.203(2)	687.3(1)

The deviation in the unit cell volume is 2.8 Å^3. According to Table S4 and Fig. S6 this difference in the unit cell volume corresponds to a temperature uncertainty between both

measurements of around 20 K. Since the powder sample used within this study was measured in a closed capillary with a temperature measurement above the capillary, and not directly at the sample could explain systematic errors in the sample temperature. Furthermore, it is not clear how the measurement of Rheingold & Hampden-Smith (2015) was carried out, hence it is difficult to judge from where the temperature mismatch results. The deviations of the lattice parameters is in average around 0.3 % to the lattice parameters of this study. While a and c are larger in the determination by Rheingold & Hampden-Smith (2015), the lattice parameter b was determined to be smaller than in our experiment. The deviation of the monoclinic angle given in this study and by Rheingold & Hampden-Smith (2015) is 0.45 %. However, the temperature change in this range involve a change of the monoclinic angle from $\beta > 90^\circ$ to $\beta < 90^\circ$ while in a standard setting, the monoclinic angle should be chosen to be $\beta \geq 90^\circ$. From the fractional coordinates given by Rheingold & Hampden-Smith (2015), it can be assumed that the monoclinic angle is the complementary[1] one of the monoclinic angle determined within this study, but the deviations for both possibilies are in the range of the deviations of the other lattice parameters. To facilitate the comparison, in Table S2 the same set of atoms chosen to define the asymmetric unit. The deviations between the fractional coordinates, the bond lengths and bond angles determined by Rheingold & Hampden-Smith (2015) and the values given in this study (Fig. S3 and Table S2) are very small and lie in the scatter of the deviations given in Table 1.

[1]The complementary angle of the unit cell determined by Rheingold & Hampden-Smith (2015) is $180^\circ - \beta = 89.797(2)^\circ$.

Table S2. *Comparison of the fractional coordinates, bond lengths and bond angles of the non-hydrogen atoms of diethylaminoalane from this study and from Rheingold & Hampden-Smith (2015).*

Atom Label	This study $x\ y\ z$	By Rheingold & Hampden-Smith (2015) $x\ y\ z$	Distance between both atoms / Å
N1	0.63442(28) 0.99081(21) 0.12835(29)	0.6336(2) 0.9923(1) 0.1318(2)	0.032(3)
C1	0.78016(19) 0.91096(11) 0.13193(20)	0.7735(3) 0.9091(2) 0.1346(4)	0.058(3)
C2	0.65640(19) 1.06186(11) 0.28800(19)	0.6552(4) 1.0658(2) 0.2894(5)	0.052(3)
C3	0.83310(18) 1.12205(11) 0.29266(19)	0.8376(3) 1.1197(2) 0.2946(4)	0.047(3)
C4	0.76494(19) 0.84991(11) 0.30853(19)	0.7722(3) 0.8433(2) 0.3089(4)	0.101(3)
Al1	0.39074(31) 0.93866(21) 0.1042(4)	0.38894(9) 0.93667(7) 0.1042(1)	0.029(3)

Bond lengths / Å

Fragment	This study from X-ray powder diffraction	By Rheingold & Hampden-Smith (2015)
Al1-N1	1.933(4)	1.946(2)
Al1'-N1	1.932(3)	1.953(2)
Al1 · · · Al1'	2.740(4)	2.757(1)

Bond angles / °

Fragment	This study from X-ray powder diffraction	By Rheingold & Hampden-Smith (2015)
N1-Al1-N1	90.1(2)	90.01(7)
Al1-N1-Al1'	89.9(2)	89.99(7)

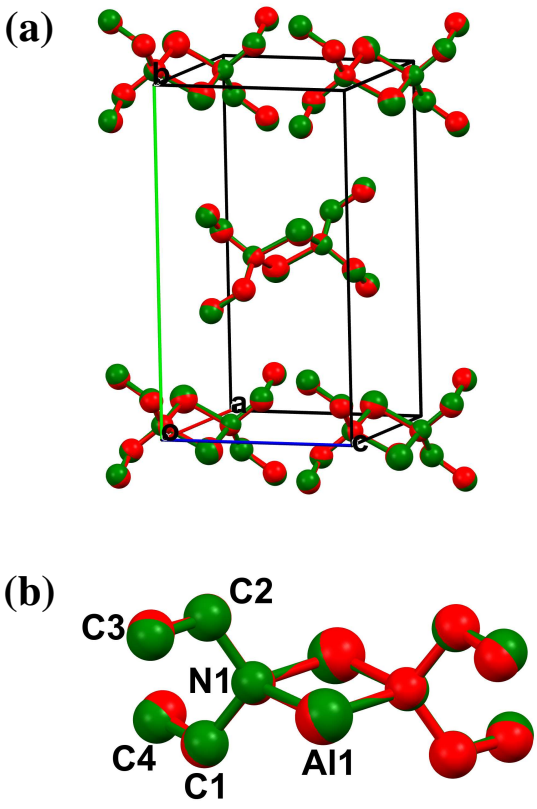

Fig. S3. Overlay of the crystal structure (a) and the molecular structure (b) of diethylaminoalane from Rheingold & Hampden-Smith (2015) (in green) with the molecular structure of this study (red).

2. Temperature dependent Measurements

Table S4. *Results of the Rietveld refinement of the X-ray powder diffraction data from laboratory measurements at different temperatures.*

T / K	a / Å	b / Å	c / Å	β / °	V / Å^3	R_{wp} / %
313	7.4134(3)	12.9843(6)	7.3010(4)	90.837(5)	702.70(4)	9.43
293	7.4020(2)	12.9663(3)	7.2878(2)	90.660(2)	699.41(3)	6.73
273	7.3936(3)	12.9522(5)	7.2721(3)	90.487(4)	696.37(4)	7.31
253	7.3848(3)	12.9379(4)	7.2592(3)	90.316(4)	693.56(3)	6.75
233	7.3752(2)	12.9229(4)	7.2456(3)	90.152(4)	690.57(3)	6.44
213	7.3646(2)	12.9095(4)	7.2318(2)	89.976(4)	687.56(3)	7.42
193	7.3547(4)	12.8953(6)	7.2174(4)	89.797(5)	684.50(5)	10.53
173	7.3466(4)	12.8849(6)	7.2071(4)	89.650(5)	682.22(4)	9.30
153	7.3370(3)	12.8770(6)	7.1957(3)	89.495(5)	679.81(4)	8.47

Table S5. *Coefficients for the polynomials given in equations 1, 2, 3, 4 and 5.*

	a
a_0 =	$7.264(2)$ Å
a_1 =	$4.76(6) \times 10^{-4}$ ÅK^{-1}
	b
b_0 =	$12.824(9)$ Å
b_1 =	$1.7(8) \times 10^{-4}$ ÅK^{-1}
b_2 =	$1.1(2) \times 10^{-6}$ ÅK^{-2}
	c
c_0 =	$7.120(7)$ Å
c_1 =	$3.9(6) \times 10^{-4}$ ÅK^{-1}
c_2 =	$6(1) \times 10^{-7}$ ÅK^{-2}
	β
β_0 =	$88.34(5)$ °
β_1 =	$6.9(5) \times 10^{-3}$ °K^{-1}
β_2 =	$3.2(9) \times 10^{-6}$ °K^{-2}
	V
V_0 =	$663(1)$ Å^3
V_1 =	$9(1) \times 10^{-2}$ Å^{3}K^{-1}
V_2 =	$1.1(2) \times 10^{-4}$ Å^{3}K^{-2}

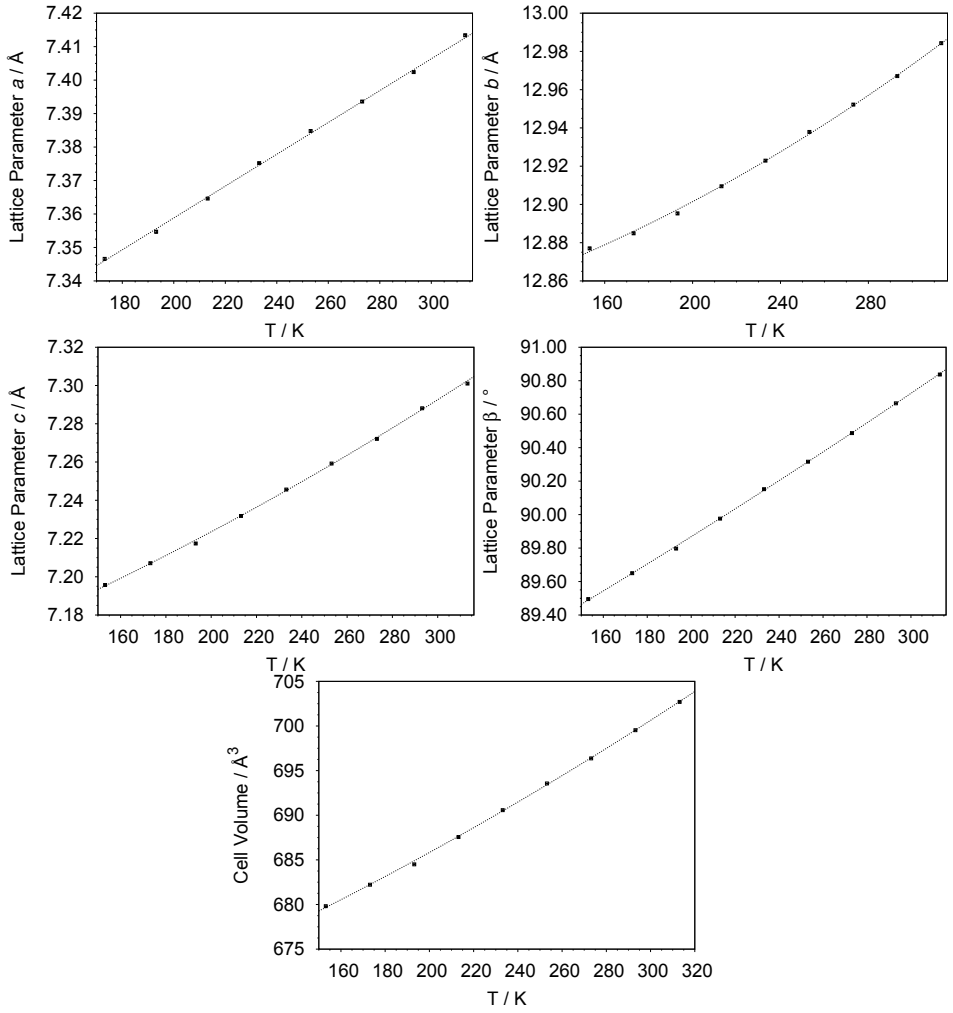

Fig. S6. Change of the lattice parameters a, b, c, β and the unit cell volume in dependence the temperature.

References

Rheingold, A. & Hampden-Smith, M., (2015). Privat Communication to CSD (CSD code DUSNAI00, CCDC 1437508) .