Supplementary Information

for

Crystal structure of sodium ethoxide (C_2H_5ONa), unravelled after a 180 years

by

Maurice Beske, Lukas Tapmeyer and Martin U. Schmidt*

Content:

1. Synthesis

All experimental procedures were performed under Ar atmosphere using Schlenk techniques.

Experiment 1: Phase mixtures

0.35 g of Na (15 mmol) were added to 10 ml of water-free ethanol (170 mmol) and stirred under argon atmosphere for 1.5 hours. The excess ethanol was removed under vacuum at room temperature, resulting in a white residue. This residue was stored under argon at room temperature at ambient pressure, whereby the residue deliquesced. The process of evaporation under vacuum, yielding a solid product, and subsequent storage under argon, was repeated until the product no longer liquefied under argon.

The product was transferred to a 1.0 mm glass capillary and sealed under argon. The X-ray powder pattern (Fig. S1) showed a phase mixture, containing the solvent-free phase **1** and the disolvate (**2**).

Experiment 2: Phase mixtures

0.35 g of Na (15 mmol) were added to 10 ml of water-free ethanol (170 mmol) and stirred under argon atmosphere for 1.5 hours. The excess ethanol was distilled off at ambient pressure, resulting in a solid product.

The product was transferred to a 1.0 mm glass capillary and sealed under argon. The X-ray powder pattern (Fig. S2) showed a phase mixture, containing **1**, **2** and phase **4** of unknown composition.

Experiment 3: Phase **1**

0.34 g (15 mmol) of sodium were added to 10 ml of water-free ethanol (170 mmol) and was allowed to react for 30 minutes at room temperature under argon atmosphere. The solution was heated to 50 °C and the excess ethanol was removed under vacuum over the course of 30 minutes. The product was dried at 50 °C under vacuum for further three hours, gently crushed with a glass rod under argon atmosphere and dried for one additional hour under vacuum at 50 °C. On treatment with argon at room temperature and ambient pressure, the white powder remained unchanged.

A sample was transferred to a 1.0 mm glass capillary and sealed under slightly reduced pressure. The X-ray powder diagram (Fig. S3) showed that the sample consists of the solvent-free phase **1**.

Determination of the chemical composition of **1**:

The stoichiometry of **1** was confirmed by decomposition of the powder with aqueous hydrochloric acid. The resulting amount of NaCl was determined gravimetrically.

The resulting amount of ethanol was determined by ^{1}H-NMR, using methanol as internal standard (measurement in D_2O).

20 mg of the product from experiment 3 were used. The measured amounts of NaCl and ethanol were compared to the theoretical amounts of the solvent-free NaOEt and a hypothetical mono-solvate NaOEt*EtOH:

Table S1. Composition of **1** as determined by decomposition experiments and analysis of gravimetric data and NMR data.

	n_{NaCl} [mmol]	n_{EtOH} [mmol]
measured	0.31	0.29
NaOEt (theo.)	0.29	0.29
NaOEt*EtOH (theo.)	0.18	0.35

Experiment 4: Phase mixtures

0.34 g of Na (15 mmol) were added to 10 ml of water-free ethanol (170 mmol) and stirred under argon atmosphere for three hours. The excess ethanol was removed under vacuum at ca. 30 °C, resulting in a white residue. This residue was dried *in vacuo* at room temperature until the product no longer liquefied under argon.

The product was transferred to an open 1.0 mm glass capillary. The X-ray powder pattern (Fig. S4) showed a phase mixture, containing the solvent-free phase **1**, the disolvate (**2**) and the phases **3** and **4** of unknown composition.

Experiment 5: Phase mixtures

0.3 g of Na (13 mmol) were added to 10 ml of water-free ethanol (170 mmol) and stirred under argon atmosphere for three hours. The excess ethanol was distilled off under vacuum at room temperature, resulting in a white residue. This residue was dried *in vacuo* until the product no longer liquified under argon.

The product was filled between polyacetate films under air and instantaneously transferred to the powder diffractometer and measured immediately. The X-ray powder pattern (Fig. S5) showed a phase mixture, containing the disolvate (**2**), and the phase **4** of unknown composition.

Experiment 6: Reaction of **1** with ethanol

A sample of **1** was transferred to a 0.7 mm glass capillary (resulting in a volume of roughly 30 µl of NaOEt sample, corresponding to about 15 µg or 0.2 µmol), mixed with approx. 50 µl of ethanol (roughly 0.9 µmol) and sealed under slightly reduced pressure (argon atmosphere).

The powder diagram (Fig. S6) showed peaks of the phases **2** and **4**.

Experiment 7: Single-crystals of $C_2H_5ONa * 2\ C_2H_5OH$ (**2**)

0.34 g of Na (15 mmol) were added to 5 ml of water-free ethanol. After reacting for 30 min a gel was formed. Excess Na was removed. After storing the gel for 3 months at room temperature, it decomposed into a brownish solution and colorless needles of **2**.

2. X-ray powder diffraction and phase analysis

All samples were measured in glass capillaries (diameter 1.0 mm) in transmission mode on a STOE-STADI-P diffractometer equipped with a Ge(111) monochromator and a position-sensitive detector unless deviating parameters are given. Cu-Kα_1 radiation (λ = 1.5406 Å) was used. The capillaries were spun during the measurement.

For phase analyses, a 2θ range of 3-40° was used. For the structure determination from powder data, a range of $2\theta = 2$ to 80° was measured. All measurements were performed at room temperature. The numbers 1, 2, 3 and 4 correspond to the phases C_2H_5ONa (**1**), $C_2H_5ONa * 2\ C_2H_5OH$ (**2**), and the phases **3** and **4** of unknown composition.

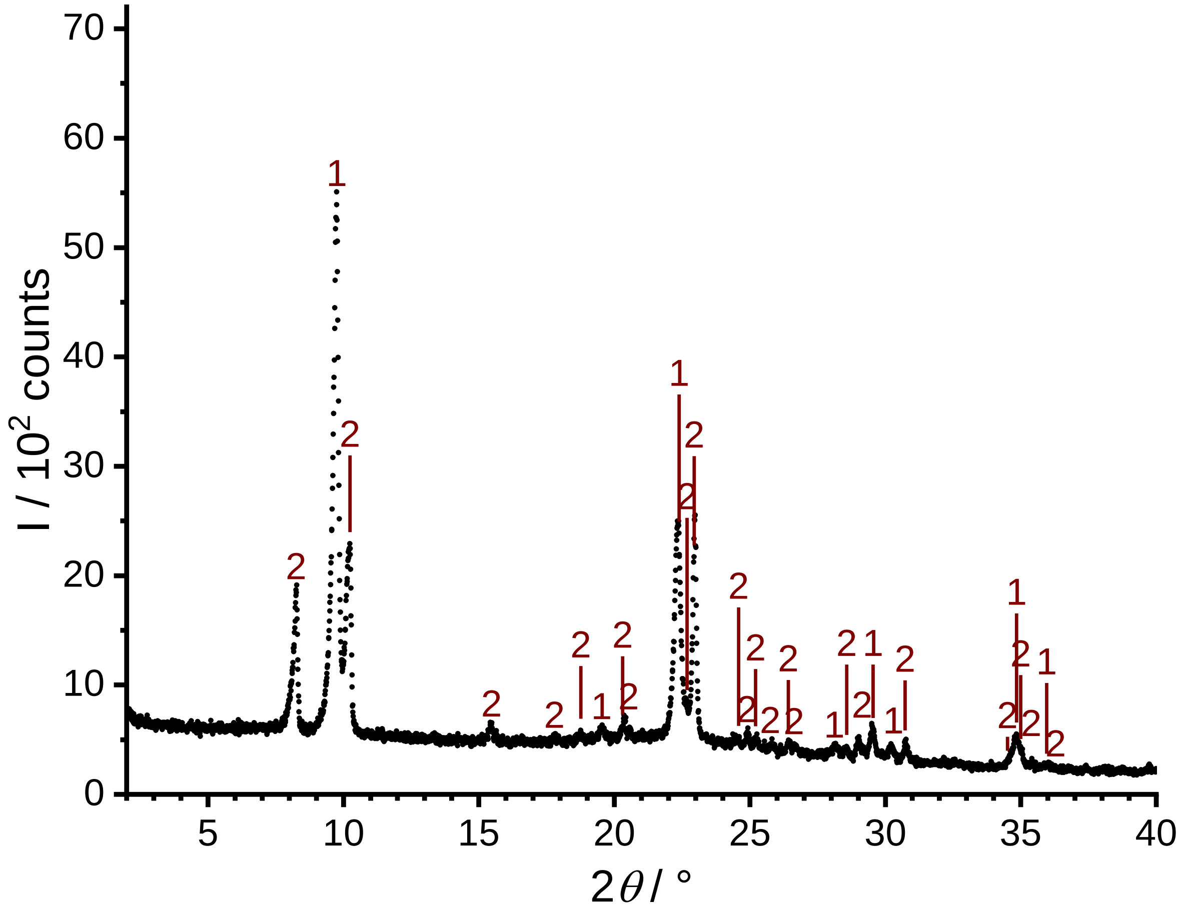

Fig. S1. Powder diagram of the product of the synthesis and solvent removal at room temperature *in vacuo* (experiment 1).

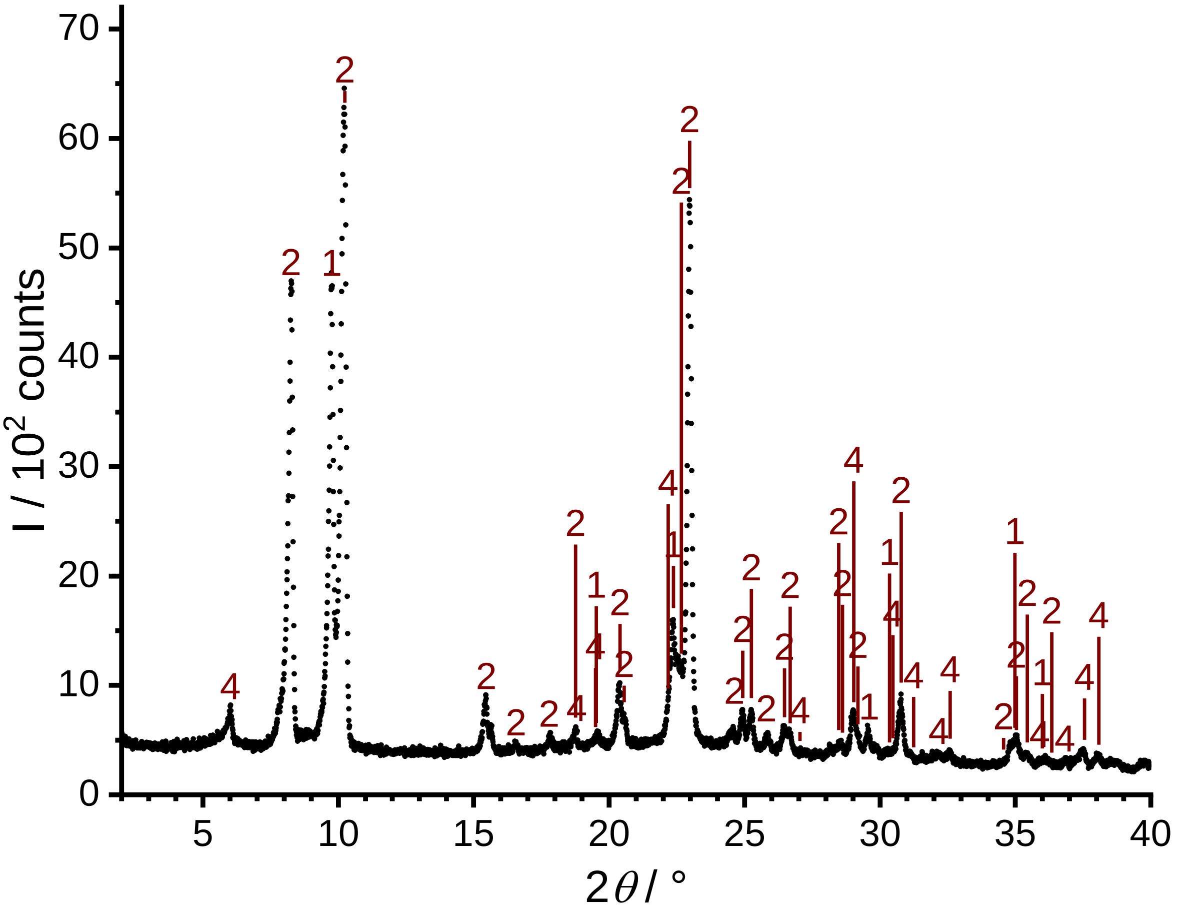

Fig. S2. Powder diagram of the product of the synthesis at room temperature with subsequent solvent removal by distillation (experiment 2).

<u>Phase composition</u>

The phase composition of the samples from experiment 1, its repetition and experiment 2 have been analysed for their contents regarding phase **1** and **2** by means of the Rietveld method.

The composition of the sample from experiment 1 was determined as roughly 56 % **1** and 44 % **2,** while a sample from its repetition experiment (about the same conditions) contained 86 % **1** and only 14 % **2**.

Experiment 2 yielded a proportion of **1** to **2** of about 17 to 83, disregarding the presence of **4**.

During these refinements, the room temperature cell parameters of **2** were refined to a = 11,667(18) Å, b = 5,196(8) Å, c = 17,95(3) Å and β = 103,53(16)° (R_{wp} roughly 6 %).

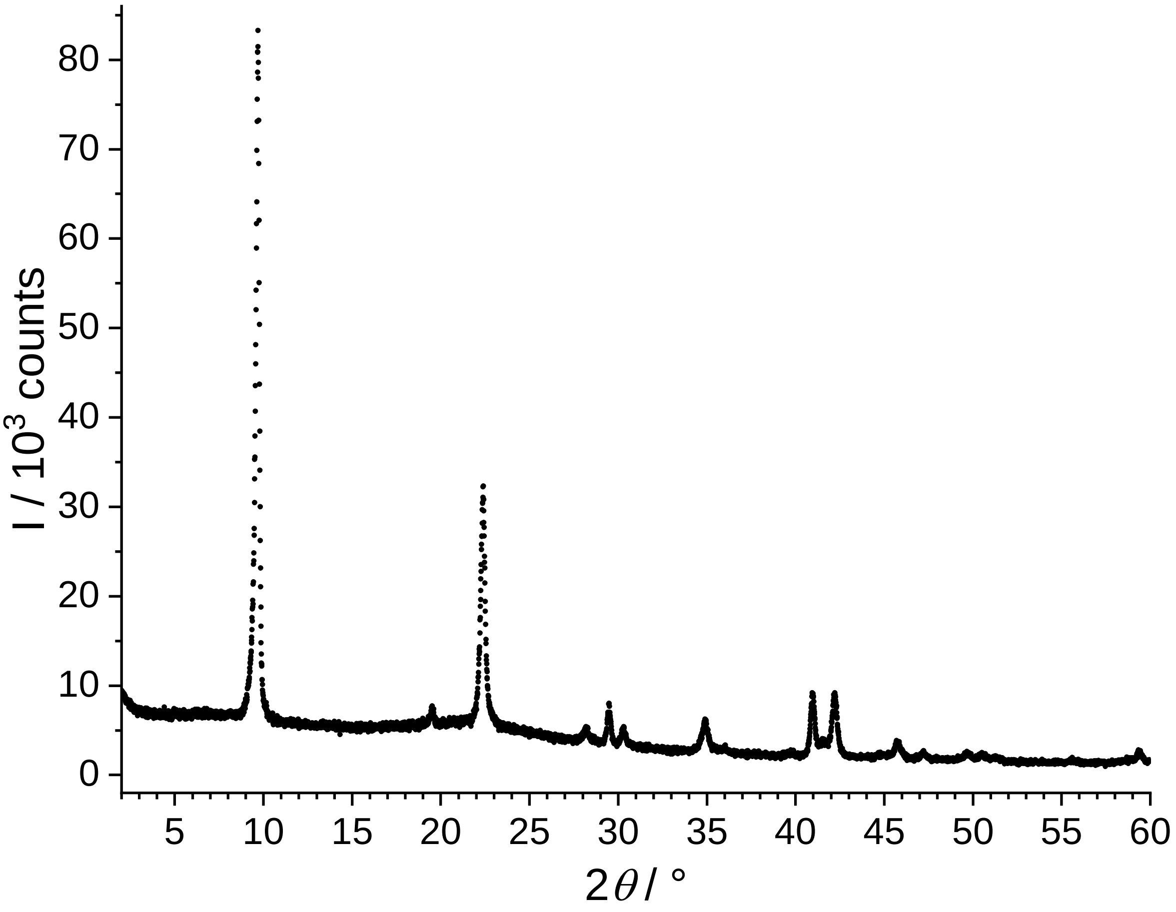

Fig. S3. Powder diagram of the product of the synthesis and careful solvent removal at 50 °C (experiment 3). Identified as pure solvent-free $NaOC_2H_5$ (**1**).

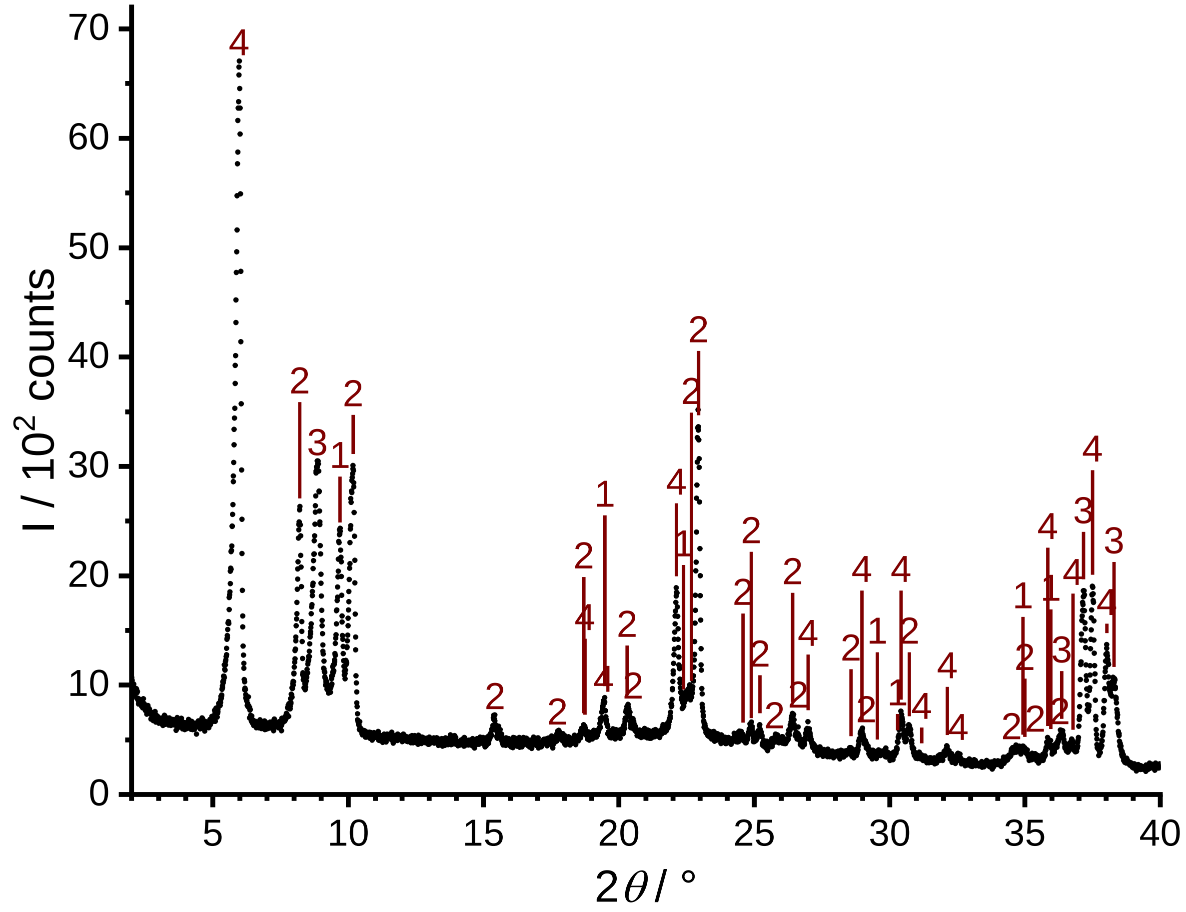

Fig. S4. Powder diagram of the product of the synthesis at room temperature and solvent removal at 30 °C. Measurement in an open capillary (contact with air; experiment 4).

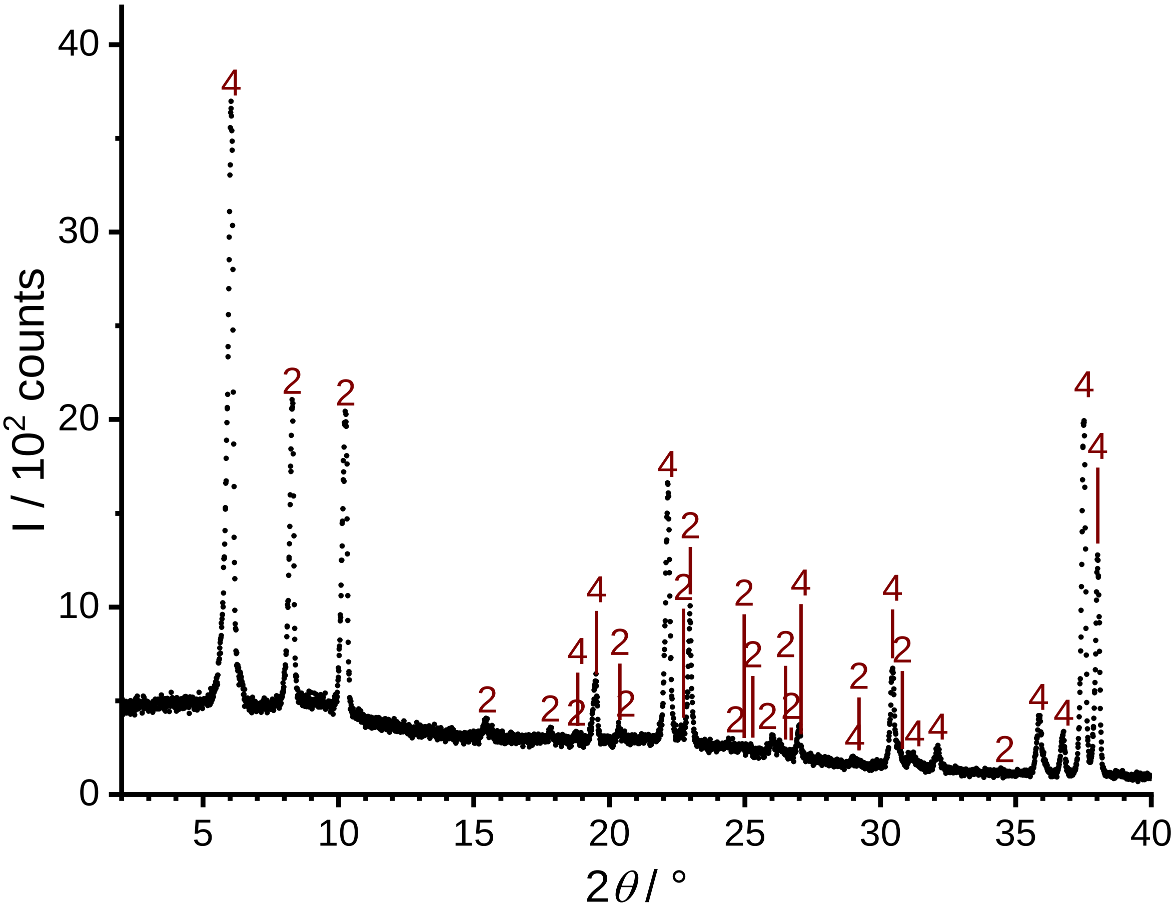

Fig. S5. Powder diagram (measured between polyacetate films) of the product of the synthesis and solvent removal at room temperature with subsequent exposure to air (experiment 5).

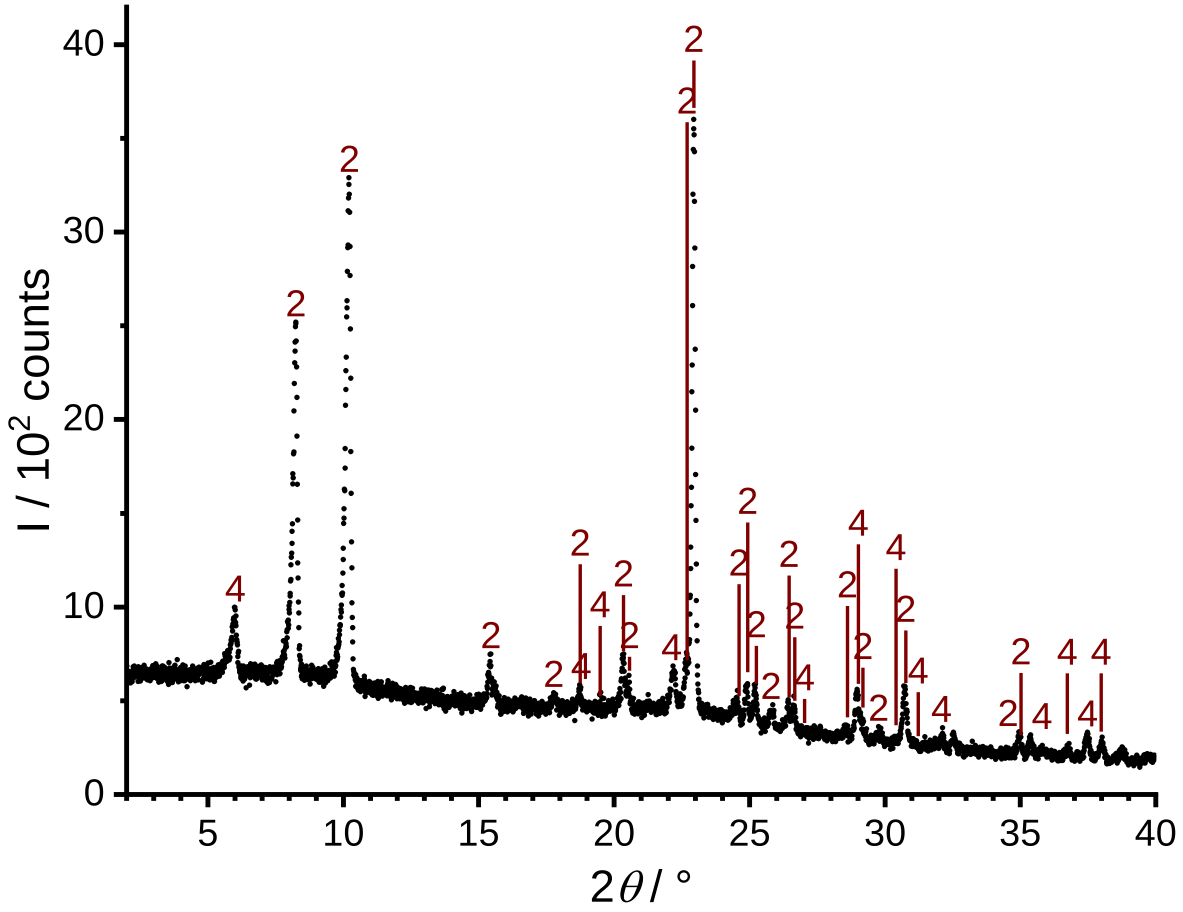

Fig. S6. Powder diagram of the product of the reaction of **1** with an excess of ethanol in a sealed 0.7 mm capillary (experiment 6).

2. IR-spectra

For C_2H_5ONa (**1**), the absence of ethanol was confirmed by IR spectroscopy. The IR spectra of **1** (Fig. S7) and of pure ethanol (Fig. S7) were measured in KBr using a Shimadzu IRAffinity-1S. Measuring spectra of the pure substances on an Specac diamond ATR top yielded no deviating information.

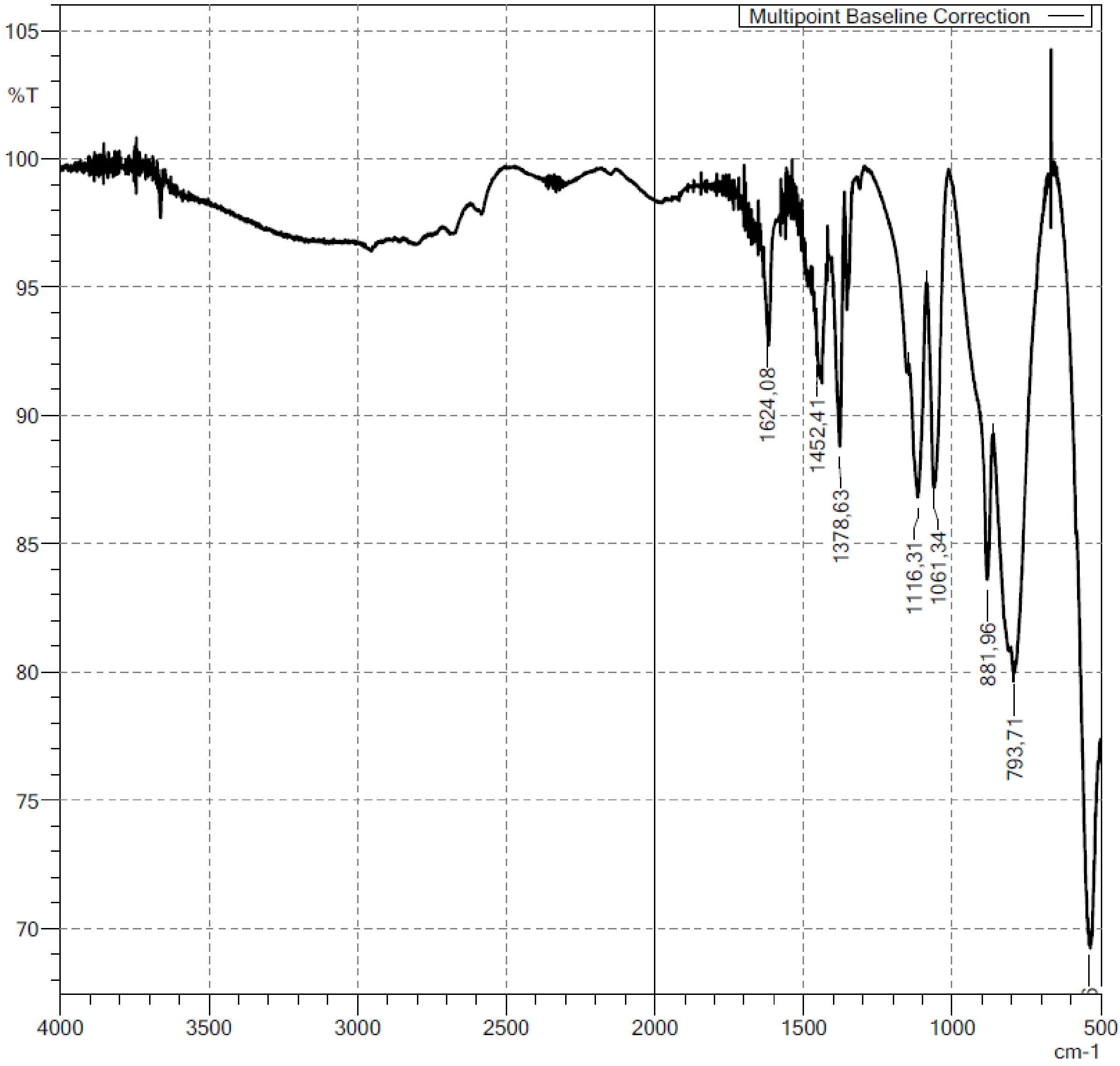

Fig. S7. IR spectrum of NaOEt (**1**)

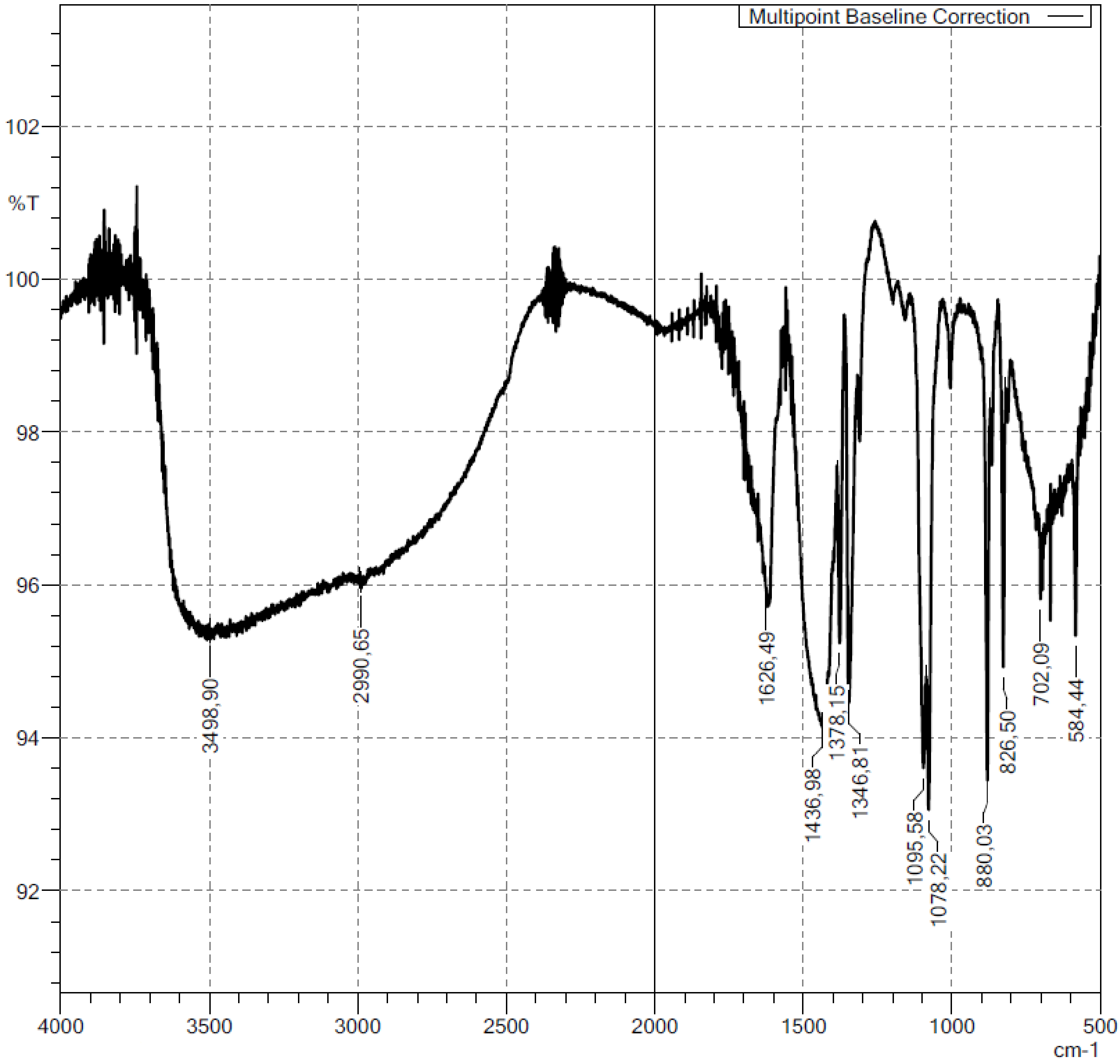

Fig. S8. IR spectrum of ethanol

4. Crystal structure of C_2H_5ONa (1)

Table S2. Crystallographic data of C_2H_5ONa (**1**) from the Rietveld refinement.

	C_2H_5ONa
CCDC number	1943793
MW /g·mol^{-1}	68.05
Crystal system	tetragonal
Space group (No.)	$P\,\overline{4}\,2_1\,m$ (113)
a /Å	4.41084(4)
b /Å	4.41084(4)
c /Å	9.06779(17)
α /°	90
$ß$ /°	90
γ /°	90
V /Å^3	176.418(5)
Z, Z'	2, 1/4
D_{calc} /Mg·m^{-3}	1.281
T /K	298
Radiation type	Cu-$K\alpha_1$
Wavelength /Å	1.5406
2θ range /°	2-80
R_p /%	2.33
R_wp /%	3.39
R_exp /%	2.14
GOF	1.58
R_p' /% [a]	13.29
R_{wp}' /% [a]	13.37
R_{exp}' /% [a]	8.45

a) R', R_wp' and R_p' values are background-corrected data.

Table S3. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for C_2H_5ONa (**1**)

	x	y	z	B_{iso}
Na1	0	0	0	3.18(7)
O2	0	0.5	-0.0810(3)	1.50(8)
C3	0.049(4)	0.549(4)	-0.2264(11)	3.7(5)
C4	-0.142(3)	0.358(3)	-0.328(2)	6.3(6)
H5	0.26(2)	0.51(2)	-0.249(5)	4.4(6)
H6	-0.357(14)	0.398(13)	-0.309(8)	7.6(8)
H7	-0.093(9)	0.407(9)	-0.430(6)	7.6(8)

Table S4. Bond lengths [Å] and angles [°] for C_2H_5ONa (**1**)

Na1-O2	2.3246(9)
O2-C3	1.35(11)
C3-C4	1.50(3)
C3-H5	0.98(9)
C4-H6	0.98(6)
C4-H7	0.98(6)
O2-C3-C4	114(2)
O2-C3-H5	109(3)
C4-C3-H5	109(4)
C3-C4-H6	110(4)
C3-C4-H7	109(4)
H6-C4-H7	110(5)

5. Crystal structure of C_2H_5ONa * 2 C_2H_5OH (2)

Single-crystals for data collection were mounted in sealed glass capillaries. During the measurement, the sample was held at -38(2) °C.

Single crystal data were collected on a Bruker Smart three-circle diffractometer equipped with an Incoatec IµS Cu microfocus source with mirror optics and an APEX CCD detector. Data collection and reduction were performed with APEX3[1]. The crystal structure was solved by direct methods using SHELXT[2] and refined with SHELXL[3]. The crystal quality was limited and did not allow the location of the positions of the H atoms of the OH groups experimentally. The compound contains one $C_2H_5O^-$ anion and two C_2H_5OH molecules. According to crystallochemical considerations, the bridging C_2H_5O fragment was assigned to be the $C_2H_5O^-$ anion, and the terminal C_2H_5O fragments to be the C_2H_5OH molecules. All H atoms were set to chemically sensible positions. OH protons were set according to the O-H...O hydrogen bonds. Subsequently, all H atoms bonded to C atoms were refined using a riding model with C-H distances constrained to 0.98 Å. Their isotropic displacement parameters were set to $U_{\mathrm{iso}}(\mathrm{H}) = 1.5\ \mathrm{U}_{\mathrm{eq}}(\mathrm{C})$ for methyl H atoms and $1.2\ \mathrm{U}_{\mathrm{eq}}(\mathrm{C})$ for methylene groups. For the H atoms of the methyl groups, free rotation about their local threefold axis was allowed. The coordinates of H atoms bonded to O atoms were refined with the O-H distances constrained to 0.83 Å. Their isotropic displacement parameters were coupled to the equivalent isotropic displacement parameters of the parent O atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{O})$. All non-H atoms were refined anisotropically. The C–C bonds within the ethyl groups are rather short, which points to an orientational disorder of the ethyl groups. However, the limited data quality did not allow further investigations. Difference-map plots performed with the final data indicate that the ethanolic H atoms bonded to O1E and O4E are correctly placed. *We thank Referee 4 for highlighting this point.*

---

[1] APEX3 Madison, Wisconsin: Bruker AXS Inc.
[2] G.M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3-8.
[3] G.M. Sheldrick, *Acta Cryst.* **2015**. *C71*, 3-8

Table S5. Experimental details for C_2H_5ONa * 2 C_2H_5OH (**2**).

Crystal data	
CCDC number	1943794
Chemical formula	$C_2H_5O^{-}\cdot Na^{+}\cdot 2(C_2H_6O)$
M_r	160.18
Crystal system, space group	Monoclinic, $P\ 2_1/n$ (No. 14)
Temperature (K)	238(2)
a, b, c (Å)	11.622 (6), 5.1926 (9), 17.682 (6)
α, β, γ (°)	90, 104.08 (3), 90
V (Å^3)	1035.0 (7)
Z, Z'	4, 1
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.01
Crystal size (mm)	0.8 × 0.08 × 0.02
Data collection	
Diffractometer	Bruker Smart three-circle diffractometer with microsource tube and Apex2 detector
Absorption correction	Multi-scan *SADABS2014*/5 Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.270, 0.749 (affected by glass capillary)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5735, 1124, 488
R_{int}	0.317
θ_{max} (°)	59.9
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.561
Refinement	
$R[F^2 > 2\sigma(F^2)]$	0.084
$wR(F^2)$	0.271
S	0.98
No. of reflections	1124
No. of parameters	95
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.20

Computer programs: Bruker *APEX3* v2016.1-0, SHELXT 2014/5 (Sheldrick, 2014), *SHELXL2018*/3 (Sheldrick, 2018), SHELXLE, *Mercury*, *ORTEPIII*.

Table S6. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for C_2H_5ONa * 2 C_2H_5OH (**2**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Na1	0.3114(2)	0.7601(4)	0.69554(13)	0.0968(13)
O1	0.3260(5)	0.6034(8)	0.8211(3)	0.0968(17)
C2	0.4470(15)	0.569(3)	0.8675(8)	0.223(7)
H2A	0.486266	0.735958	0.867099	0.267
H2B	0.440773	0.541507	0.921175	0.267
C3	0.5097(17)	0.424(4)	0.8568(11)	0.323(13)
H3A	0.485107	0.254984	0.870052	0.485
H3B	0.588323	0.461864	0.888617	0.485
H3C	0.511020	0.427293	0.802141	0.485
O1E	0.2865(4)	0.4120(8)	0.6207(3)	0.118(2)
H1E	0.243170	0.312748	0.638022	0.141
C2E	0.2525(13)	0.409(2)	0.5373(7)	0.223(7)
H2EA	0.280388	0.245300	0.520599	0.267
H2EB	0.165653	0.403895	0.522063	0.267
C3E	0.2847(13)	0.583(2)	0.4976(6)	0.249(7)
H3EA	0.250898	0.551456	0.442631	0.373
H3EB	0.370539	0.584575	0.507726	0.373
H3EC	0.257385	0.748905	0.511828	0.373
O4E	0.4418(5)	1.0603(9)	0.6740(3)	0.132(2)
H4E	0.389362	1.132.212	0.640316	0.159
C5E	0.5533(16)	1.087(3)	0.6544(13)	0.270(9)
H5EA	0.537092	1.113.465	0.597908	0.324
H5EB	0.590469	1.245.078	0.679145	0.324
C6E	0.6255(16)	0.917(4)	0.6709(13)	0.309(11)
H6EA	0.697417	0.967393	0.656196	0.31(8)
H6EB	0.593936	0.761376	0.643216	0.461
H6EC	0.643210	0.885733	0.726623	0.461

Table S7. Bond lengths [Å] and angles [°] for C_2H_5ONa * 2 C_2H_5OH (**2**)

Na1-O1E	2.217(5)
Na1-O4E	2.269(6)
Na1-O1	2.331(5)
O1-C2	1.456(14)
C2-C3	1.096(15)*
C2-H2A	0.9800
C2-H2B	0.9800
C3-H3A	0.9700
C3-H3B	0.9700
C3-H3C	0.9700
O1E-C2E	1.431(10)
O1E-H1E	0.8300
C2E-C3E	1.257(13)*
C2E-H2EA	0.9800
C2E-H2EB	0.9800
C3E-H3EA	0.9700
C3E-H3EB	0.9700
C3E-H3EC	0.9700
O4E-C5E	1.428(14)
O4E-H4E	0.8300
C5E-C6E	1.203(15)*
C5E-H5EA	0.9800
C5E-H5EB	0.9800
C6E-H6EA	0.9700
C6E-H6EB	0.9700
C6E-H6EC	0.9700
O1E-Na1-O4E	117.1(2)
O1E-Na1-O1	104.64(18)
O4E-Na1-O1	120.2(2)
C2-O1-Na1	114.6(7)
C3-C2-O1	125.3(19)
C3-C2-H2A	105.9
O1-C2-H2A	106.0
C3-C2-H2B	106.0
O1-C2-H2B	106.0
H2A-C2-H2B	106.3
C2-C3-H3A	109.4
C2-C3-H3B	109.5
H3A-C3-H3B	109.5
C2-C3-H3C	109.5
H3A-C3-H3C	109.5
H3B-C3-H3C	109.5
C2E-O1E-Na1	126.0(5)
C2E-O1E-H1E	109.5
Na1-O1E-H1E	106.8
C3E-C2E-O1E	121.5(11)
C3E-C2E-H2EA	107.0
O1E-C2E-H2EA	107.0
C3E-C2E-H2EB	107.0
O1E-C2E-H2EB	107.0
H2EA-C2E-H2EB	106.7
C2E-C3E-H3EA	109.5
C2E-C3E-H3EB	109.5
H3EA-C3E-H3EB	109.5
C2E-C3E-H3EC	109.5
H3EA-C3E-H3EC	109.5
H3EB-C3E-H3EC	109.5
C5E-O4E-Na1	142.2(8)
C5E-O4E-H4E	109.5
Na1-O4E-H4E	91.5
C6E-C5E-O4E	119.4(17)
C6E-C5E-H5EA	107.5
O4E-C5E-H5EA	107.5
C6E-C5E-H5EB	107.5
O4E-C5E-H5EB	107.5
H5EA-C5E-H5EB	107.0
C5E-C6E-H6EA	109.5
C5E-C6E-H6EB	109.5
H6EA-C6E-H6EB	109.5
C5E-C6E-H6EC	109.5
H6EA-C6E-H6EC	109.5
H6EB-C6E-H6EC	109.5

* affected by disorder of the ethyl groups

Table S8. Anisotropic displacement parameters (Å^2) for C_2H_5ONa * 2 C_2H_5OH (**2**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Na1	0.136(3)	0.0692(18)	0.090(2)	-0.0011(13)	0.0356(18)	-0.0061(15)
O1	0.102(4)	0.097(3)	0.086(4)	0.005(3)	0.011(3)	0.007(3)
C2	0.200(16)	0.274(17)	0.145(11)	-0.025(11)	-0.051(11)	0.095(12)
C3	0.229(19)	0.41(3)	0.27(2)	-0.101(19)	-0.047(14)	0.145(18)
O1E	0.200(5)	0.078(3)	0.082(4)	-0.003(2)	0.048(3)	-0.021(3)
C2E	0.44(2)	0.136(9)	0.082(9)	-0.002(6)	0.051(10)	-0.054(11)
C3E	0.406(19)	0.195(12)	0.147(11)	0.061(9)	0.072(11)	-0.059(13)
O4E	0.119(5)	0.107(4)	0.180(5)	0.004(3)	0.055(4)	-0.006(3)
C5E	0.191(17)	0.208(17)	0.46(3)	0.057(16)	0.178(17)	0.012(12)
C6E	0.202(18)	0.27(2)	0.52(3)	0.09(2)	0.20(2)	0.055(15)