**Bruker Quest Instruments:**

**Bruker Quest with Mo radiation (before May 2020):**

Single crystals of ??? were coated with ??? and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon100 area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) at ??? K.

**Bruker Quest with Cu radiation (before May 2020):**

Single crystals of ??? were coated with ??? and quickly transferred to the goniometer head of a Bruker Quest diffractometer with kappa geometry, an I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror for monochromatization, a Photon-II area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu Kα radiation (λ = 1.54178 Å) at ??? K.

**Bruker Quest with Mo radiation (after May 2020):**

Single crystals of ??? were coated with ??? and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon II area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) at ??? K.

**Bruker Quest with Cu radiation (after May 2020):**

Single crystals of ??? were coated with ??? and quickly transferred to the goniometer head of a Bruker Quest diffractometer with kappa geometry, an I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon-III C14 area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu Kα radiation (λ = 1.54178 Å) at ??? K.

**Common to both Bruker Quest instruments:**

Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3 [1] and SADABS [2]. The space groups were assigned using XPREP within the SHELXTL suite of programs [3,4] and solved by direct methods using ShelXS [4] or dual methods using ShelXT [5] and refined by full matrix least squares against F2 with all reflections using Shelxl2018 [6] using the graphical interface Shelxle [7]. If not specified otherwise H atoms attached to carbon, boron and nitrogen atoms as well as hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic and alkene C-H and CH2 and alkyne C-H moieties, and to 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH2 and CH3 moieties, respectively. B-H bond distances were constrained to 1.00 Å for pyramidal (sp3 hybridized) R3B-H moieties. N-H bond distances were constrained to 0.88 Å for planar (sp2 hybridized) N-H, N-H+ and NH2 groups. N-H bond distances were constrained to 0.91 Å for pyramidal (sp3 hybridized) ammonium NH2+ and NH3+ groups. O-H distances of alcohols were constrained to 0.84 Å. Methyl CH3, ammonium NH3+ and hydroxyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. H atoms of pyramidalized R2NH and RNH2 units were refined and N-H distances were restrained to 0.88(2) Å. Water H atom positions were refined and O-H distances were restrained to 0.84(2) Å. Where necessary, water H⋅⋅⋅H distances were restrained to 1.36(2) Å, and H atom positions were further restrained based on hydrogen bonding considerations. Uiso(H) values were set to a multiple of Ueq(C) with 1.5 for CH3, NH3+ and OH, and 1.2 for C-H, CH2, B-H, N-H and NH2 units, respectively.

Additional data collection and refinement details, including description of disorder (where present) can be found in the Supporting Information. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC nnnnnn contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

[1] Bruker (2019). Apex3 v2019.1-0, SAINT V8.40A, Bruker AXS Inc.: Madison (WI), USA.

[2] Krause, L., Herbst-Irmer, R., Sheldrick, G.M. & Stalke, D. (2015). J. Appl. Cryst. 48, 3-10.

[3] SHELXTL suite of programs, Version 6.14, 2000-2003, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA

[4] Sheldrick, G.M. A short history of SHELX. Acta Crystallogr A. 2008, 64(1), 112–122.

[5] Sheldrick, G. M., "SHELXT--Integrated space-group and crystal-structure determination", Acta Crystallogr A. 2015, A71, 3-8.

[6] a) Sheldrick, G.M. University of Göttingen, Germany, 2018. b) Sheldrick, G.M. Crystal structure refinement with SHELXL. Acta Crystallogr Sect C Struct Chem. 2015, 71(1), 3–8.

[7] Hübschle, C.B., Sheldrick, G.M. & Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL. J. Appl. Crystallogr. 2011, 44(6), 1281–1284.

Longer (more detailed) example:

Single crystals of the investigated compounds were coated with a trace of Fomblin oil and were transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a Mo Kα wavelength (λ = 0.71073 Å) sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, and a Photon100 area detector (after May 2020: Photon II area detector), or onto a Bruker Quest diffractometer with kappa geometry, a Cu Kα wavelength (λ = 1.54178 Å) I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror for monochromatization, and a Photon II area detector (after May 2020: Photon III C14 area detector). Both instruments were equipped with an Oxford Cryosystems low temperature device and examination and data collection were performed at 150 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3 [1] and SADABS [2]. The space groups were assigned using XPREP within the SHELXTL suite of programs [3,4] and solved by direct methods using ShelXS [4] or dual methods using ShelXT [5] and refined by full matrix least squares against F2 with all reflections using Shelxl2018 [6] using the graphical interface Shelxle [7]. H atoms attached to carbon, boron and nitrogen atoms as well as hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic and alkene C-H and CH2 and alkyne C-H moieties, and to 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH2 and CH3 moieties, respectively. B-H bond distances were constrained to 1.00 Å for pyramidal (sp3 hybridized) R3B-H moieties. N-H bond distances were constrained to 0.88 Å for planar (sp2 hybridized) N-H, N-H+ and NH2 groups. N-H bond distances were constrained to 0.91 Å for pyramidal (sp3 hybridized) ammonium NH2+ and NH3+ groups. O-H distances of alcohols were constrained to 0.84 Å. Methyl CH3, ammonium NH3+ and hydroxyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. H atoms of pyramidalized R2NH and RNH2 units were refined and N-H distances were restrained to 0.88(2) Å. Water H atom positions were refined and O-H distances were restrained to 0.84(2) Å. Where necessary, water H⋅⋅⋅H distances were restrained to 1.36(2) Å, and H atom positions were further restrained based on hydrogen bonding considerations. Uiso(H) values were set to a multiple of Ueq(C) with 1.5 for CH3, NH3+ and OH, and 1.2 for C-H, CH2, B-H, N-H and NH2 units, respectively.

Additional data collection and refinement details, including description of disorder (where present) can be found in the Supporting Information. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC nnnnnn contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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[6] a) Sheldrick, G.M. University of Göttingen, Germany, **2018**. b) Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr Sect C Struct Chem.* **2015**, *71(1)*, 3–8.

[7] Hübschle, C.B., Sheldrick, G.M. & Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011**, *44(6)*, 1281–1284.

**Retired Instruments:**

**Rigaku R-axis diffractometer:**

Single crystal X-ray measurements were conducted on a Rigaku Rapid II curved image plate diffractometer with a Cu-Kα X-ray microsource (λ = 1.54178 Å) with a laterally graded multilayer (Goebel) mirror for monochromatization. Single crystals were mounted on Mitegen microloop mounts using a trace of mineral oil and cooled in-situ to ???(2) K for data collection. Data were collected using the dtrek option of CrystalClear-SM Expert 2.1 b32 [1]. Data were processed using HKL3000 [2] and data were corrected for absorption and scaled using Scalepack [2]. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs [3]. They were refined by full matrix least squares against *F*2 with all reflections using Shelxl2014 [4] with the graphical interface Shelxle [5].

If not specified otherwise H atoms attached to carbon, boron and nitrogen atoms as well as hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic and alkene C-H and CH2 and alkyne C-H moieties, and to 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH2 and CH3 moieties, respectively. B-H bond distances were constrained to 1.00 Å for pyramidal (sp3 hybridized) R3B-H moieties. N-H bond distances were constrained to 0.88 Å for planar (sp2 hybridized) N-H, N-H+ and NH2 groups. N-H bond distances were constrained to 0.91 Å for pyramidal (sp3 hybridized) ammonium NH2+ and NH3+ groups. O-H distances of alcohols were constrained to 0.84 Å. Methyl CH3, ammonium NH3+ and hydroxyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. H atoms of pyramidalized R2NH and RNH2 units were refined and N-H distances were restrained to 0.88(2) Å. Water H atom positions were refined and O-H distances were restrained to 0.84(2) Å. Where necessary, water H⋅⋅⋅H distances were restrained to 1.36(2) Å, and H atom positions were further restrained based on hydrogen bonding considerations. Uiso(H) values were set to a multiple of Ueq(C) with 1.5 for CH3, NH3+ and OH, and 1.2 for C-H, CH2, B-H, N-H and NH2 units, respectively.

Additional data collection and refinement details, including description of disorder (where present) can be found in the Supporting Information. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC nnnnnn contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

[1] Rigaku Corp., The Woodlands, Texas, USA.

[2] Otwinowski Z, Minor W., Processing of X-ray diffraction data collected in oscillation mode. *Methods Enzymol.* **1997**, *276*, 307–326.

[3] a) SHELXTL suite of programs, Version 6.14, 2000-2003, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA) b) Sheldrick GM. A short history of SHELX. *Acta Crystallogr A.* **2008**, *64(1)*, 112–122.

[4] a) Sheldrick GM. University of Göttingen, Germany, **2014**. b) Sheldrick GM. Crystal structure refinement with SHELXL. *Acta Crystallogr Sect C Struct Chem.* **2015**, *71(1)*, 3–8.

[5] Hübschle CB, Sheldrick GM, Dittrich B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011**, *44(6)*, 1281–1284.

**Nonius Kappa CCD diffractometer:**

Crystals were transferred to the goniometer head of a Nonius KappaCCD diffractometer equipped with a graphite crystal incident beam monochromator and examined with Mo Kα radiation (λ = 0.71073 Å). They were cooled in-situ to ???(2) K and examined with Mo Kα radiation (λ = 0.71073 Å). Data were collected using the Nonius Collect software [1], processed using HKL3000 [2] and data were corrected for absorption and scaled using Scalepack [2]. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs [3]. They were refined by full matrix least squares against *F*2 with all reflections using Shelxl2014 [4] with the graphical interface Shelxle [5].

If not specified otherwise H atoms attached to carbon, boron and nitrogen atoms as well as hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic and alkene C-H and CH2 and alkyne C-H moieties, and to 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH2 and CH3 moieties, respectively. B-H bond distances were constrained to 1.00 Å for pyramidal (sp3 hybridized) R3B-H moieties. N-H bond distances were constrained to 0.88 Å for planar (sp2 hybridized) N-H, N-H+ and NH2 groups. N-H bond distances were constrained to 0.91 Å for pyramidal (sp3 hybridized) ammonium NH2+ and NH3+ groups. O-H distances of alcohols were constrained to 0.84 Å. Methyl CH3, ammonium NH3+ and hydroxyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. H atoms of pyramidalized R2NH and RNH2 units were refined and N-H distances were restrained to 0.88(2) Å. Water H atom positions were refined and O-H distances were restrained to 0.84(2) Å. Where necessary, water H⋅⋅⋅H distances were restrained to 1.36(2) Å, and H atom positions were further restrained based on hydrogen bonding considerations. Uiso(H) values were set to a multiple of Ueq(C) with 1.5 for CH3, NH3+ and OH, and 1.2 for C-H, CH2, B-H, N-H and NH2 units, respectively.

Additional data collection and refinement details, including description of disorder (where present) can be found in the Supporting Information. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC nnnnnn contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

[1] Nonius (1998). Collect Users Manual, Nonius Delft, The Netherlands.

[2] Otwinowski Z, Minor W., Processing of X-ray diffraction data collected in oscillation mode. *Methods Enzymol.* **1997**, *276*, 307–326.

[3] a) SHELXTL suite of programs, Version 6.14, 2000-2003, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA) b) Sheldrick GM. A short history of SHELX. *Acta Crystallogr A.* **2008**, *64(1)*, 112–122.

[4] a) Sheldrick GM. University of Göttingen, Germany, **2014**. b) Sheldrick GM. Crystal structure refinement with SHELXL. *Acta Crystallogr Sect C Struct Chem.* **2015**, *71(1)*, 3–8.

[5] Hübschle CB, Sheldrick GM, Dittrich B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011**, *44(6)*, 1281–1284.