Porphyrinoids

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Dithiaethyneporphyrin: An Atypical [18]Triphyrin(4.1.1) Frame for Contracted Porphyrins**

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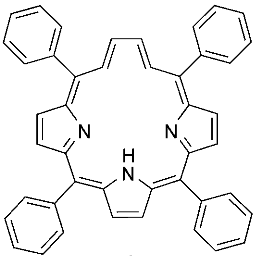
The aza-deficent porphyrin 5,10,15,20-tetraaryl-21-vacataporphyrin (butadieneporphyrin, [18]triphyrin(6.1.1); **1**) is an annulene–porphyrin hybrid.[1] In principle, vacataporphyrin **1** (paradoxically expanded porphyrin)[2–4] can be considered as a seminal molecule for the subclass of triphyrins, which are distinguished by the fact that they contain only three pyrrole or pyrrole-like rings, linked by two sp^2-hybridized *meso* carbon atoms to form the tripyrrolic brace. The macrocyclic structure of triphyrins is completed by a single chain of sp^2- and/or sp-hybridized carbon atoms. Besides vacataporphyrin, only [15]triphyrin(1.1.3), which was obtained serendipitously during the condensation of triisopropylsilyl propynal with 3,4-diethylpyrrole, meets the criterion outlined above.[5] Alternatively, the replacement of the six inner protons of [18]annulene by three oxygen, sulfur, or NH (NR) groups, or some combination of the three, as explored originally by Badger et al., leads to heteroatom-bridged annulenes **2**; that is, [18]triphyrin(2.2.2) or [18]heterotriphyrin(2.2.2).[6–8]



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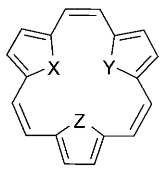
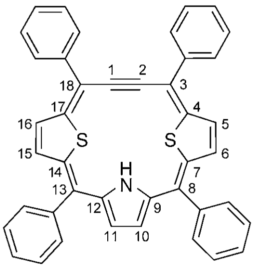


X, Y, Z = S, O, NH, NR

2

Herein, we report the synthesis and characterization of 3,8,13,18-tetraphenyl-19,21-dithiaethyneporphyrin (H(S_2-ETPP); **3**). This porphyrin derivative is a novel type of contracted heteroporphyrin related to putative [18]triphyrin-(4.1.1) with an acetylene moiety embedded in the macrocyclic framework. It introduces a unique structural pattern for contracted porphyrins,[2,4] created by fusing the structural motifs of 21,23-dithiaporphyrin and acetylene.



3

The synthetic strategy for **3** (Scheme 1) resembles the [3+1] approach applied to prepare porphyrins, heteroporphyrins, and carbaporphyrinoids.[9] Retrosynthetic analysis led to the identification of 1,4-di(2-thienyl)-1,4-diphenyl-2-butyne (**7**) as the fundamental building block for the construction of **3**. Eventually, dithiaethyneporphyrin **3** was formed through a condensation reaction that is similar to the [3+1] procedure for porphyrins, although the *meso* carbon atoms here originated from **9** rather than the usual monopyrrolic fragment (12.7 % yield).

The electronic spectrum of **3** (Figure 1) shows a distinct intense Soret-like band at $\lambda = 448$ nm accompanied by less-intense Q bands at 518, 553, 646, and 725 nm, resembling the spectroscopic features of aromatic 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin, S_2TPP.[10] The ^{1}H NMR spectrum of **3** also resembled that of S_2TPP[10] and displayed resonances at positions consistent with an aromatic structure: porphyrinoid **3** retains macrocyclic aromaticity through an 18-π-electron delocalization motif. The scalar coupling detected between NH20 and the β-pyrrolic protons H10 and H11 confirms the molecular structure of **3** (Figure 2). The ^{13}C NMR chemical shifts of the four-carbon linker derived from 2-butyne reveals a symmetric structure, with $\delta = 116.8$ ppm for C1 and C2 and $\delta = 111.9$ ppm for C3 and C18.

Two canonical structures of **3** define 18-π-electron macrocyclic delocalization pathways (Scheme 2). Accordingly, the

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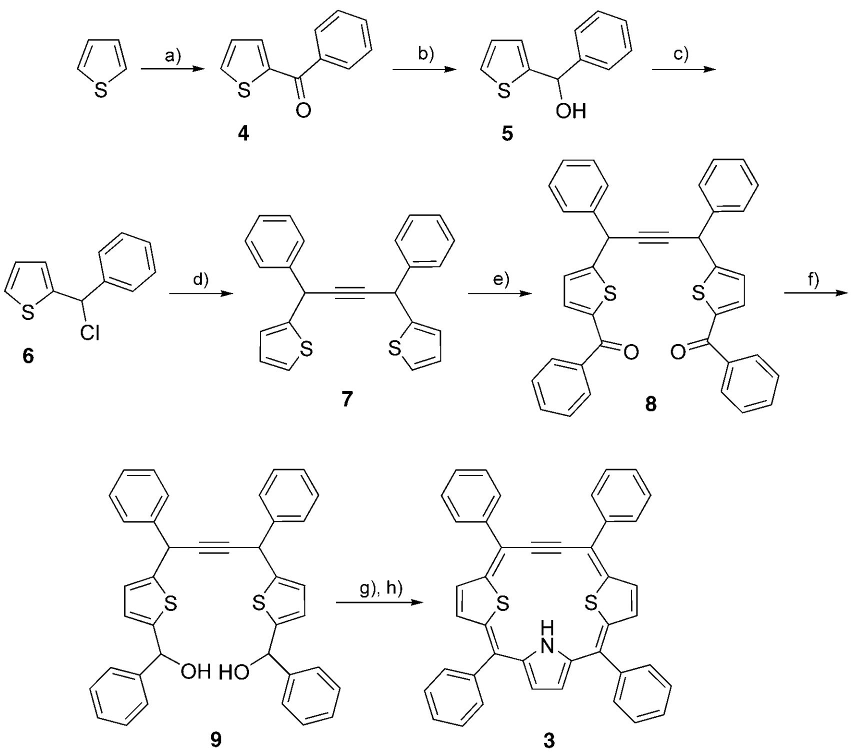


Scheme 1. Synthesis of dithiaethyneporphyrin **3**: a) PhCOCl, $AlCl_3$, CH_2Cl_2, RT→reflux, 6 h; b) $NaBH_4$, THF/MeOH (3:2 *V*/*V*); c) conc. HCl; d) BrMgC≡CMgBr, CuCl, THF, reflux, 2 h; e) PhCOCl, $AlCl_3$, CH_2Cl_2, room temperature, 14 h; f) $NaBH_4$, THF/MeOH (3:2 *V*/*V*); g) pyrrole, CH_3SO_3H, room temperature, 1 h; h) Et_3N, DDQ, room temperature, 1.5 h. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

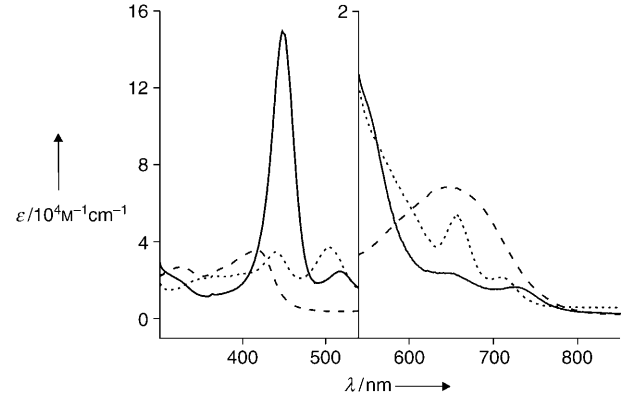
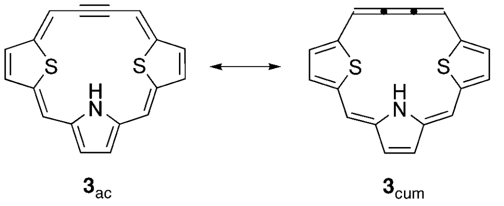


Figure 1. The electronic spectra of **3** (——, CH_2Cl_2), **10** (-----, $CHCl_3$), and **11** (– – –, CH_2Cl_2).



Scheme 2. Canonical structures of **3**.

electronic structure of **3** can be described as reflecting a combination of acetylene (=C–C≡C–C=) and cumulene (–C=C=C=C–) character of the C18-C1-C2-C3 fragment. The relevant chemical shift values of carbon atoms for acetylene or cumulene units attached adjacent to aryl or 2-thienyl moieties were considered for comparison. The sp-hybridized carbon atoms of intermediate **7** gave a ^{13}C NMR signal at $\delta = 84.4$ ppm, that is, in the $\delta = 70$–95 ppm range typical for acetylene. Similarly, the ^{13}C NMR chemical shifts of cumulene fragments vary over quite a wide range: $\delta = 140.5$ ppm for tetra(2-thienyl)butatriene,[11] $\delta = 152.0$ ppm for tetraphenylbutatriene,[12] and $\delta = 134.5$ ppm for 6,7,18,19-tetradehydro-tetrathia[24]annulene(4.0.4.0) (some admixture of the acetylenic structure was suggested for the latter structure).[13] Thus the ^{13}C NMR chemical shifts of **3** point out that canonical structure $\mathbf{3}_{ac}$ and $\mathbf{3}_{cum}$ (ac = acetylene; cum = cumulene) contribute to the overall electronic structure, although the acetylene character of the C_{sp}–C_{sp} moiety prevails. The detected chemical shifts of **3** were fairly typical for acetylene–cumulene porphyrinoids[14,15] and acetylene–cumulene annulenes.[16]

The structure of **3** was determined by X-ray diffraction studies and is shown in Figure 3.[17] The S···S distance is short

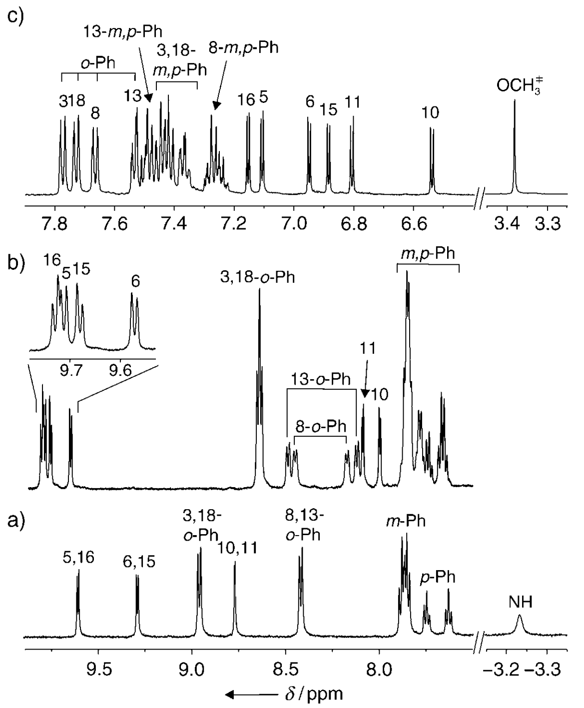


Figure 2. ^{1}H NMR spectra of a) **3** ($CDCl_3$, 298 K), b) **10** ($CDCl_3$, 240 K), and c) **11** (CD_2Cl_2, 298 K). Peak labels correspond to systematic position numbering or denote proton groups such as *o*,*m*,*p* positions of the *meso*-phenyl groups. Chemical shift values are relative to TMS (tetramethylsilane: $\delta = 0$ ppm). (‡): the intensity of the OCH_3 signal has been decreased by a factor of 5.

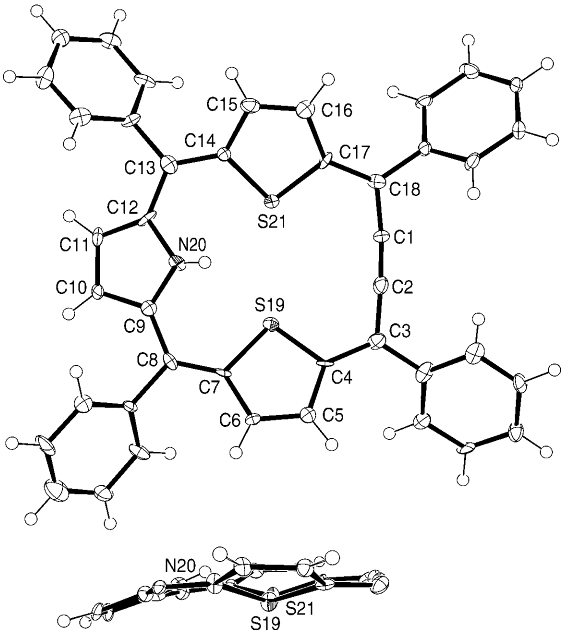
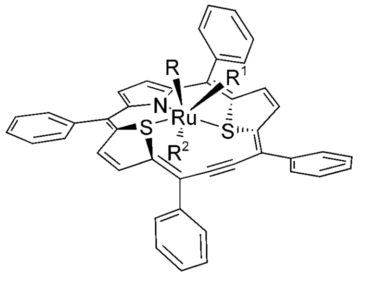


Figure 3. Crystal structure of dithiaethyneporphyrin **3**: a) top and b) side view (phenyl groups are omitted for clarity). The vibrational ellipsoids represent 50% probability. The bond lengths in the $C_{sp^2}C_{sp}C_{sp}C_{sp^2}$ (C18-C1-C2-C3) unit are 1.390(9) Å, 1.231(10) Å, and 1.418(10) Å, respectively. The dihedral angles between the plane defined by the four *meso* carbon atoms (C3, C8, C13, C18) and the planes of the five-membered rings are as follows: thiophene(S19) −19.0(2)°, pyrrole 17.6(3)°, thiophene(S21) −18.0(3)°.

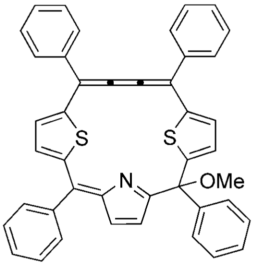
(3.113(3) Å), and only a small number of compounds that contain such close sulfur–sulfur contacts have been reported.[13,18–20] The C_{sp^2}-C_{sp}-C_{sp}-C_{sp^2} butyne moiety reveals a slight distortion from linearity, showing a bowlike deformation directed outward of the macrocycle (C18-C1-C2: 174.0(9)°; C1-C2-C3: 176.6(9)°).

Treatment of **3** with $[Ru_3(CO)_{12}]$ in chlorobenzene resulted in formation of $[(S_2ETPP)Ru^{II}(CO)_2Cl]$ (**10**), as confirmed by high-resolution mass spectrometry. The ^{1}H NMR spectrum of complex **10** revealed a lowering of symmetry relative to **3**. The geometry of **10** as inferred from the ^{1}H NMR spectroscopic pattern (Figure 2b) reflects the balance between constraints of the macrocyclic ligand and the coordination requirement of ruthenium(II) for octahedral geometry. Dithiaethyneporphyrin **3** has to distort to accommodate Ru^{II} binding. Consequently, the two thiophene rings are severely tilted in opposite directions with respect to the macrocyclic plane to allow the pyramidal side-on coordination of ruthenium(II), in a similar manner as detected for $[(S_2TPP)Ru^{II}Cl_2]$.[21] The puckering of dithiaethyneporphyrin and the difference in coordination above and below the porphyrin plane explains the observed lowering of symmetry of **10** relative to **3**. The 2-butyne fragment is not involved in coordination, as the ^{13}C chemical shifts of non-equivalent atoms C1 and C2 in **10** ($\delta = 111.1$ and 113.7 ppm) resemble those for **3**.

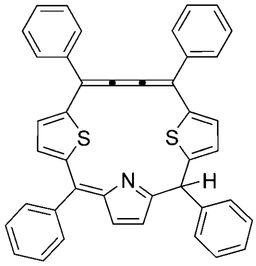


10: R, R^1, R^2 equal Cl and two CO

Dithiaethyneporphyrin **3** reacts regioselectively with methanol (or ethanol) in the presence of silver acetate to produce *iso*-8-methoxy-3,8,13,18-tetraphenyl-19,21-dithiaethyneporphyrin (**11**). Derivative **11** is related to a feasible non-aromatic isomer of **3**, that is, *iso*-dithiaethyneporphyrin, *iso*-**3**. The UV/Vis spectrum of **11** confirms a loss of aromaticity, as evident by the smaller extinction coefficients (Figure 1). The ^{1}H NMR resonances of **11** were detected in the region that is typical for the conjugated but non-aromatic system. The ^{13}C NMR shift of C8 ($\delta = 83.1$ ppm) is consistent with its tetrahedral geometry, whereas those of atoms C1 and C2 ($\delta = 143.8$ and 147.2 ppm) comply with a cumulenic structure. Treatment of **11** with gaseous HCl results in partial recovery of **3**.



11



iso-**3**

In conclusion, dithiaethyneporphyrin—a new aromatic contracted porphyrinoid—has been synthesized and characterized and displays the unique features of an [18]dithiatriphyrin(4.1.1) frame.

Experimental Section

3: Pyrrole (0.11 mL, 1.58 mmol), **9** (0.9 g, 1.55 mmol), and freshly distilled CH_2Cl_2 (750 mL) were placed in a 1-L flask. Nitrogen was bubbled through the solution for 30 min, then CH_3SO_3H (0.2 mL, 3.1 mmol) was added, and the mixture was stirred in the dark for 1 h under N_2. Triethylamine (0.49 mL, 3.5 mmol) and DDQ (2.1 g, 9.3 mmol) were added and the solution was stirred for a further 1.5 h. The solvent was partly evaporated, and the reaction mixture was purified by chromatography on silica gel. The first orange-brown fraction (product **2**) was eluted with dichloromethane and repurified through a second chromatographic procedure on silica gel with hexane/benzene (1:1 *V*/*V*) as eluant. Product **2** was recrystallized from CH_2Cl_2/CH_3OH (120 mg, 12.7%); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 448 (5.2), 518 (4.4), 553 (4.1), 646 (3.4), 725 nm (3.3); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, TMS): $\delta = 9.61$, 9.29 (AB, $^3J(H,H) = 4.4$ Hz, 4H; H5,16, H6,15), 8.96 (d, $^3J(H,H) = 7.7$ Hz, 4H; 3,18-*o*-Ph), 8.77 (d, $^4J(H,H) = 1.5$ Hz, 2H; H10,11), 8.42 (d, $^3J(H,H) = 7.7$ Hz, 4H; 8,13-*o*-

Ph), 7.88 (t, ^{3}J(H,H) = 7.7 Hz, 4H; 3,18-*m*-Ph), 7.85 (t, ^{3}J(H,H) = 7.7 Hz, 4H; 8,13-*m*-Ph), 7.75 (t, ^{3}J(H,H) = 7.7 Hz, 2H; 8,13-*p*-Ph), 7.63 (t, ^{3}J(H,H) = 7.7 Hz, 2H; 3,18-*p*-Ph), −3.24 ppm (br s, 1H; NH); HR-MS (ESI): *m*/*z* calcd for $C_{42}H_{27}N^{32}S_2$ [M^+]: 609.1585; found: 609.1607; elemental analysis: calcd (%) for $C_{42}H_{27}NS_2$: C 82.27, H 4.65, N 2.50, S 10.45; found: C 82.72, H 4.46, N 2.30, S 10.52.

10: Compound **3** (20 mg, 0.033 mmol) and [$Ru_3(CO)_{12}$] (0.84 g, 1.32 mmol) in freshly distilled chlorobenzene (20 mL) were heated at reflux for 4 h under N_2. The solvent was evaporated to dryness and the residue was purified by chromatography on silica gel. After an initial orange-red fraction (recovered **3**) had been eluted with hexane/benzene (1:1 *V*/*V*), elution with benzene led to a second brown fraction, which was collected and identified as **10**. The second fraction was purified through a second column (silica gel with hexane/benzene (1:3 *V*/*V*) and recrystallized from $CHCl_3/CH_3OH$ to yield the title product (9 mg, 34%). UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 367 (4.3), 440 (4.5), 505 (4.6), 659 (3.8), 711 nm (3.4); ^{1}H NMR (500 MHz, $CDCl_3$, 240 K, TMS): δ = 9.83, 9.78 (AB, ^{3}J(H,H) = 5.2 Hz, 2H; H15, H16), 9.81, 9.67 (AB, ^{3}J(H,H) = 5.2 Hz, 2H; H5, H6), 8.65 (m, 4H; 3,18-*o*-Ph), 8.49 (d, ^{3}J(H,H) = 7.3 Hz, 1H; 13-*o*-Ph), 8.46 (d, ^{3}J(H,H) = 7.3 Hz, 1H; 8-*o*-Ph), 8.17 (d, ^{3}J(H,H) = 7.3 Hz, 1H; 8-*o*-Ph), 8.13 (d, ^{3}J(H,H) = 7.3 Hz, 1H; 13-*o*-Ph), 8.10, 8.00 (AB, ^{3}J(H,H) = 4.1 Hz, 2H; H10, H11), 7.85 (m, 7H; *m*-Ph), 7.78 (m, 2H; 8-*p*-Ph, 13-*m*-Ph), 7.74 (t, ^{3}J(H,H) = 7.3 Hz, 1H; 13-*p*-Ph), 7.66 ppm (m, 2H; 3,18-*p*-Ph); IR (KBr): $\tilde{\nu}$ = 2065, 2012 cm^{-1} (C≡O); HR-MS (ESI): *m*/*z* calcd for $^{12}C_{44}H_{26}NO_2{}^{32}S_2{}^{35}Cl^{102}Ru$ [M^+]: 801.0311; found: 801.0428; elemental analysis: calcd (%) for $C_{44}H_{26}NO_2S_2ClRu\cdot 0.8\,CHCl_3\cdot 1.4\,CH_3OH$: C 58.92, H 3.47, N 1.49; found: C 59.10, H 3.79, N 1.10.

11: UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 325 (4.4), 415 (4.6), 649 nm (3.9); ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K, TMS): δ = 7.77 (d, ^{3}J(H,H) = 7.3 Hz, 2H; 3-*o*-Ph), 7.73 (d, ^{3}J(H,H) = 7.3 Hz, 2H; 18-*o*-Ph), 7.67 (d, ^{3}J(H,H) = 7.0 Hz, 2H; 8-*o*-Ph), 7.54 (d, ^{3}J(H,H) = 7.0 Hz, 2H; 13-*o*-Ph), 7.49 (m, 3H; 13-*m*,*p*-Ph), 7.45 (t, ^{3}J(H,H) = 7.3 Hz, 2H; 18-*m*-Ph), 7.42 (t, ^{3}J(H,H) = 7.3 Hz, 2H; 3-*m*-Ph), 7.37 (m, 2H; 3,18-*p*-Ph), 7.28 (m, 3H; 8-*m*,*p*-Ph), 7.16, 6.89 (AB, ^{3}J(H,H) = 4.0 Hz, 2H; H15, H16), 7.11, 6.95 (AB, ^{3}J(H,H) = 4.0 Hz, 2H; H5, H6), 6.81, 6.54 (AB, ^{3}J(H,H) = 4.4 Hz, 2H; H10, H11), 3.38 ppm (s, 3H; OCH_3); HR-MS (ESI): *m*/*z* calcd for $C_{43}H_{30}NO^{32}S_2$ [$M-H$]$^+$: 640.1769; found: 640.1793.

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Keywords: annulenes · aromaticity · heterocycles · NMR spectroscopy · porphyrinoids

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[17] X-ray crystal structure data for **3**·$CHCl_3$: crystals were prepared by slow diffusion of CH_3OH into a solution of **3** in $CHCl_3$ to yield dark brown crystals of $C_{42}H_{27}NS_2\cdot CHCl_3$, size $0.22 \times 0.014 \times 0.008$ mm^3, monoclinic, space group $P2_1/n$, $a = 14.726(6)$ Å, $b = 8.536(3)$ Å, $c = 27.761(9)$ Å, $\beta = 105.02(3)°$, $V = 3370(2)$ Å^3, $\rho_{calcd.} = 1.437$, $Z = 4$; Xcalibur PX κ-geometry diffractometer, $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å), $T = 100$ K, $2\theta_{max} = 153.88$; total number of reflections collected: 23091; number of independent reflections: 6527, of which 6527 were included in the refinement of 419 parameters; an analytical numeric absorption correction was applied:[22] $\mu = 3.883$ mm^{-1}, $T_{min} = 0.661$, $T_{max} = 0.972$. The structure was solved by using direct methods with SHELXS-97 and refined against $|F^2|$ using SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany, **1997**), final R_1/wR_2 indices (for $I > 2\sigma(I)$): 0.0691/0.1108; max/min residual electron density: $+0.40/-0.42$ e A^{-3}. The disordered molecule of chloroform is present. Hydrogen atoms except H20 (NH) were fixed in idealized positions using the riding model constraints. CCDC-265651 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.
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