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1:1 Co-crystal of 3-ethyl-4-methyl-3-pyrrolin-2-one and 3-ethyl-4-methyl-3-pyrroline-2,5-dione

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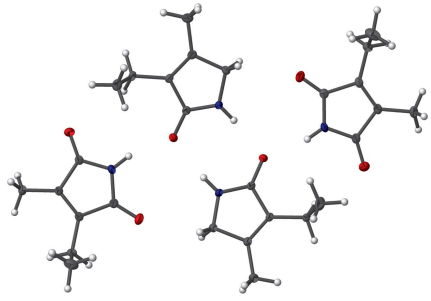
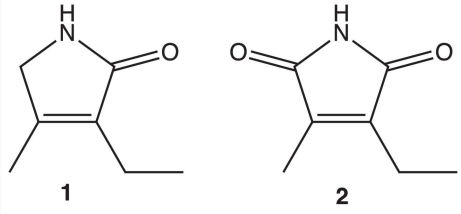
Structural data: full structural data are available from iucrdata.iucr.org

Crystallization from a 20-year-old commercial source of 3-ethyl-4-methyl-3-pyrrolin-2-one afforded 1:1 co-crystals of this compound ($C_7H_{11}NO$) with its oxidized derivative, 3-ethyl-4-methyl-3-pyrroline-2,5-dione ($C_7H_9NO_2$). The compound crystallizes in the space group $P\overline{1}$, with two molecules of each species in the asymmetric unit. These four molecules form a hydrogen-bonded tetramer with a dimer of 3-ethyl-4-methyl-3-pyrrolin-2-one as the core flanked by one molecule of the dione on each side.

3D view



Chemical scheme



Structure description

3-Ethyl-4-methyl-3-pyrrolin-2-one, $C_7H_{11}NO$ (**1**) is an α,β–unsaturated lactam derivative. It has medical applications and is used as a starting material to synthesize glimepiride, the only sulfonyl urea approved by the US Food and Drug Administration (FDA) for use with insulin to treat type 2 diabetes. (Tanwar *et al.*, 2017). We attempted to crystallize 3-ethyl-4-methyl-3-pyrrolin-2-one from a 20-year-old commercial source (Aldrich), but upon solving the structure, it was determined that the compound crystallized as a 1:1 co-crystal with its oxidized derivative, 3-ethyl-4-methyl-3-pyrrolin-2,5-dione, $C_7H_9NO_2$ (**2**), which is also known as 2-ethyl-3-methylmaleimide. The source of this maleimide is unclear, though it is reported to form through certain aerobic photoxidation pathways, for example from chlorophyls (Xian *et al.*, 2006; Kozono *et al.*, 2002), and therefore aerobic oxidation cannot be ruled out.

The asymmetric unit of the triclinic co-crystal consists of two molecules of each compound (Fig. 1). These four molecules are held together by four N—H···O hydrogen bonds, Table 1. At the center of the tetramer is a dimer of 3-ethyl-4-methyl-3-pyrrolin-2-one molecules held together by two N—H···O hydrogen bonds with N···O distances of 2.8487 (15) and 2.9222 (15) Å. The oxygen atom of each pyrrolinone unit also accepts a

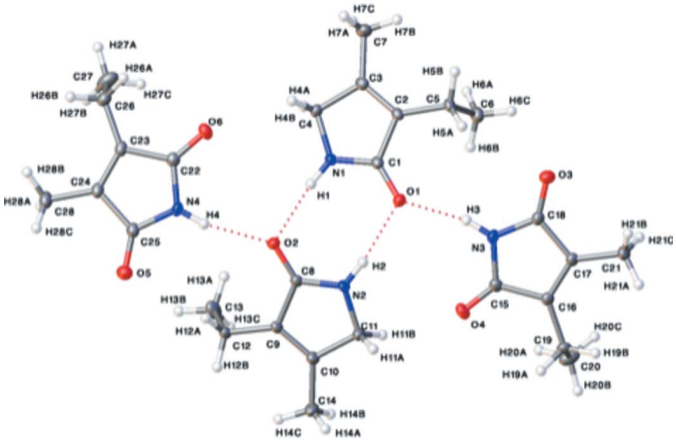


Figure 1
The asymmetric unit of the crystal contains two molecules of each component of the co-crystal, linked together by four hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level.

second hydrogen bond from the N—H unit of a maleimide molecule; these $D\cdots A$ distances are similar to those in the core, being 2.8202 (15) Å and 2.8677 (15) Å. The oxygen atoms of the maleimide molecules do not engage in hydrogen bonding – the shortest intermolecular distances to the maleimide carbonyls are long (> 2.70 Å) C—H$\cdots$O contacts.

The C═O bonds of all four molecules in the asymmetric unit are consistent with the degree of resonance delocalization of the molecule. The C═O bonds of pyrrolinone **1** are longer [1.2495 (15) and 1.2467 (15) Å] than the C═O bonds of maleimide **2** [1.2100 (16)–1.2132 (16) Å]. Correspondingly, the N—C(O) bonds of the maleimides are longer [1.3838 (17)–1.3865 (17) Å)] than the N—C(O) bonds of the pyrrolinones [1.3395 (17) and 1.3391 (17) Å].

Synthesis and crystallization

Commercial 3-ethyl-4-methyl-3-pyrrolin-2-one (Aldrich) was purchased in 1997 and stored under air at room temperature. A sample was crystallized in 2019 by slow evaporation of a dichloromethane solution at room temperature over several days. Nearly colorless blocks were obtained and data were collected on these crystals at 100 K.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

We thank Dr Mark Bezpalko for access to and maintenance of the instrument used in this study.

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O2	0.89 (2)	1.97 (2)	2.8487 (15)	173 (2)
N2—H2$\cdots$O1	0.88 (2)	2.05 (2)	2.9222 (15)	171 (2)
N3—H3$\cdots$O1	0.88 (2)	1.97 (2)	2.8202 (15)	165 (2)
N4—H4$\cdots$O2	0.86 (2)	2.03 (2)	2.8677 (15)	165 (2)

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_9NO_2{\cdot}C_7H_{11}NO$
M_r	264.32
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	10.2673 (17), 11.885 (2), 12.839 (2)
α, β, γ (°)	90.601 (3), 108.694 (2), 108.797 (2)
V (Å^3)	1393.6 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.5 × 0.4 × 0.4
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.638, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22087, 7807, 5738
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.694
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.129, 1.02
No. of reflections	7807
No. of parameters	363
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, −0.31

Computer programs: *SAINT* and *APEX2* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*b*), *SHELXL* (Sheldrick, 2015*a*) and *OLEX2* (Dolomanov *et al.*, 2009).

Funding information

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full crystallographic data

IUCrData (2019). **4**, x191209 [https://doi.org/10.1107/S2414314619012094]

1:1 Co-crystal of 3-ethyl-4-methyl-3-pyrrolin-2-one and 3-ethyl-4-methyl-3-pyrroline-2,5-dione

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3-Ethyl-4-methyl-3-pyrrolin-2-one–3-ethyl-4-methyl-3-pyrroline-2,5-dione (1/1)

Crystal data

$C_7H_9NO_2 \cdot C_7H_{11}NO$
$M_r = 264.32$
Triclinic, $P\overline{1}$
$a = 10.2673$ (17) Å
$b = 11.885$ (2) Å
$c = 12.839$ (2) Å
$\alpha = 90.601$ (3)°
$\beta = 108.694$ (2)°
$\gamma = 108.797$ (2)°
$V = 1393.6$ (4) Å^3
$Z = 4$
$F(000) = 568$
$D_x = 1.260$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4195 reflections
$\theta = 2.2$–30.4°
$\mu = 0.09$ mm^{-1}
$T = 100$ K
Block, off-white
0.5 × 0.4 × 0.4 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
$T_{min} = 0.638$, $T_{max} = 0.746$
22087 measured reflections
7807 independent reflections
5738 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 29.6°$, $\theta_{min} = 1.7°$
$h = -14 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.129$
$S = 1.02$
7807 reflections
363 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.2427P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 1. Fixed Uiso At 1.2 times of: All C(H,H) groups, All N(H) groups At 1.5 times of: All C(H,H,H) groups 2.a Secondary CH2 refined with riding coordinates: C4(H4A,H4B), C5(H5A,H5B), C19(H19A,H19B), C12(H12A,H12B), C11(H11A,H11B), C26(H26A,H26B) 2.b Idealised Me refined as rotating group: C6(H6A,H6B,H6C), C21(H21A,H21B,H21C), C28(H28A,H28B,H28C), C14(H14A,H14B, H14C), C7(H7A,H7B,H7C), C13(H13A,H13B,H13C), C20(H20A,H20B,H20C), C27(H27A, H27B,H27C)
The coordinates of the four hydrogen atoms (H1–H4) engaged in hydrogen bonds were refined while all others were treated with a riding model.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O2	0.21235 (10)	0.36055 (8)	0.67113 (8)	0.0189 (2)
O6	0.01203 (11)	0.43139 (9)	0.40166 (8)	0.0204 (2)
O4	0.75738 (11)	0.53952 (9)	1.01712 (8)	0.0227 (2)
O1	0.56722 (10)	0.62186 (9)	0.75879 (8)	0.0200 (2)
N1	0.38644 (12)	0.55072 (10)	0.58794 (9)	0.0167 (2)
H1	0.3252 (18)	0.4919 (15)	0.6090 (13)	0.020*
N3	0.83545 (13)	0.71001 (10)	0.93659 (10)	0.0184 (2)
H3	0.7591 (19)	0.6936 (14)	0.8759 (14)	0.022*
N2	0.41748 (13)	0.39669 (10)	0.82662 (9)	0.0173 (2)
H2	0.4672 (18)	0.4676 (15)	0.8144 (13)	0.021*
N4	−0.07317 (13)	0.28418 (11)	0.50433 (10)	0.0179 (2)
H4	0.0032 (19)	0.3029 (14)	0.5626 (14)	0.021*
C17	1.05941 (14)	0.79960 (12)	1.07610 (10)	0.0150 (3)
C22	−0.08165 (14)	0.34340 (12)	0.41122 (11)	0.0155 (3)
C15	0.84850 (15)	0.63481 (12)	1.01803 (11)	0.0161 (3)
C16	0.99545 (14)	0.69420 (11)	1.10621 (10)	0.0148 (3)
C4	0.35382 (14)	0.58429 (12)	0.47670 (10)	0.0160 (3)
H4A	0.261465	0.601924	0.452921	0.019*
H4B	0.346318	0.520259	0.422851	0.019*
C25	−0.19971 (14)	0.18630 (12)	0.48532 (11)	0.0165 (3)
C8	0.28393 (14)	0.33068 (11)	0.75769 (10)	0.0145 (3)
C2	0.57626 (14)	0.71910 (11)	0.59323 (11)	0.0143 (3)
C9	0.23720 (14)	0.21533 (11)	0.80256 (10)	0.0145 (3)
C1	0.51327 (14)	0.62710 (11)	0.65760 (11)	0.0146 (3)
C3	0.48329 (14)	0.69498 (12)	0.48829 (11)	0.0160 (3)
C18	0.95907 (15)	0.81199 (12)	0.96574 (11)	0.0158 (3)
C23	−0.22806 (14)	0.27622 (12)	0.32497 (11)	0.0158 (3)
C5	0.72351 (14)	0.81347 (12)	0.64460 (11)	0.0166 (3)
H5A	0.735531	0.842900	0.720704	0.020*
H5B	0.731364	0.881951	0.600889	0.020*
C10	0.34397 (15)	0.21846 (12)	0.89684 (11)	0.0181 (3)
C24	−0.29647 (14)	0.18262 (12)	0.36832 (11)	0.0160 (3)
C19	1.04928 (15)	0.63491 (12)	1.20459 (11)	0.0179 (3)
H19A	0.967578	0.594456	1.231284	0.022*
H19B	1.126080	0.696203	1.265012	0.022*
C12	0.09622 (15)	0.11766 (12)	0.74122 (11)	0.0166 (3)
H12A	0.016830	0.151805	0.716328	0.020*

H12B	0.071684	0.058196	0.791571	0.020*
C11	0.46781 (15)	0.33592 (12)	0.92045 (11)	0.0200 (3)
H11A	0.483313	0.381371	0.991025	0.024*
H11B	0.559978	0.323772	0.923819	0.024*
C6	0.84446 (15)	0.76321 (13)	0.64858 (13)	0.0217 (3)
H6A	0.837583	0.740555	0.572885	0.033*
H6B	0.833063	0.692535	0.688108	0.033*
H6C	0.940213	0.824333	0.687316	0.033*
C26	−0.27140 (16)	0.31362 (13)	0.21204 (11)	0.0205 (3)
H26A	−0.232183	0.402105	0.217677	0.025*
H26B	−0.379499	0.287546	0.180019	0.025*
C21	1.20247 (15)	0.89522 (12)	1.13460 (12)	0.0212 (3)
H21A	1.239559	0.881228	1.211939	0.032*
H21B	1.189481	0.973418	1.132249	0.032*
H21C	1.272630	0.894004	1.098176	0.032*
C28	−0.44102 (15)	0.08562 (13)	0.31799 (12)	0.0227 (3)
H28A	−0.426890	0.014964	0.290058	0.034*
H28B	−0.503616	0.113395	0.256625	0.034*
H28C	−0.487704	0.064646	0.374165	0.034*
C14	0.34989 (17)	0.12475 (13)	0.97320 (12)	0.0267 (3)
H14A	0.365796	0.158789	1.047956	0.040*
H14B	0.430505	0.096871	0.974960	0.040*
H14C	0.257235	0.057154	0.946743	0.040*
C7	0.49576 (17)	0.76137 (14)	0.39212 (12)	0.0251 (3)
H7A	0.490389	0.706904	0.331831	0.038*
H7B	0.589613	0.827669	0.414715	0.038*
H7C	0.415465	0.793187	0.366574	0.038*
C13	0.10590 (18)	0.05544 (14)	0.64105 (12)	0.0279 (3)
H13A	0.138738	0.115245	0.594465	0.042*
H13B	0.009283	−0.002138	0.598084	0.042*
H13C	0.175899	0.013167	0.666147	0.042*
C20	1.11168 (19)	0.54321 (14)	1.17583 (12)	0.0281 (3)
H20A	1.037566	0.485350	1.112993	0.042*
H20B	1.139336	0.501084	1.239994	0.042*
H20C	1.198210	0.584309	1.156019	0.042*
C27	−0.21402 (19)	0.25974 (17)	0.13569 (13)	0.0326 (4)
H27A	−0.238918	0.289768	0.063739	0.049*
H27B	−0.258790	0.172231	0.125321	0.049*
H27C	−0.107419	0.282525	0.168859	0.049*
O3	0.98077 (11)	0.89459 (9)	0.91156 (8)	0.0225 (2)
O5	−0.22727 (11)	0.11830 (9)	0.55131 (8)	0.0247 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0159 (5)	0.0195 (5)	0.0151 (5)	0.0016 (4)	0.0015 (4)	0.0072 (4)
O6	0.0182 (5)	0.0173 (5)	0.0219 (5)	0.0000 (4)	0.0078 (4)	0.0008 (4)
O4	0.0206 (5)	0.0181 (5)	0.0217 (5)	−0.0031 (4)	0.0070 (4)	0.0010 (4)

O1	0.0163 (5)	0.0203 (5)	0.0155 (5)	0.0006 (4)	0.0005 (4)	0.0057 (4)
N1	0.0146 (5)	0.0142 (5)	0.0148 (5)	−0.0004 (4)	0.0019 (4)	0.0046 (4)
N3	0.0154 (6)	0.0178 (6)	0.0132 (5)	0.0001 (5)	−0.0008 (5)	0.0016 (4)
N2	0.0161 (6)	0.0133 (5)	0.0152 (5)	−0.0011 (5)	0.0018 (4)	0.0050 (4)
N4	0.0130 (5)	0.0202 (6)	0.0131 (5)	0.0005 (5)	0.0000 (4)	0.0009 (4)
C17	0.0151 (6)	0.0147 (6)	0.0118 (6)	0.0023 (5)	0.0030 (5)	−0.0002 (5)
C22	0.0156 (6)	0.0157 (6)	0.0155 (6)	0.0053 (5)	0.0056 (5)	−0.0001 (5)
C15	0.0166 (6)	0.0165 (6)	0.0130 (6)	0.0023 (5)	0.0056 (5)	0.0006 (5)
C16	0.0157 (6)	0.0146 (6)	0.0117 (6)	0.0030 (5)	0.0038 (5)	−0.0002 (5)
C4	0.0142 (6)	0.0169 (6)	0.0128 (6)	0.0029 (5)	0.0019 (5)	0.0022 (5)
C25	0.0138 (6)	0.0158 (6)	0.0178 (6)	0.0043 (5)	0.0038 (5)	0.0007 (5)
C8	0.0150 (6)	0.0137 (6)	0.0124 (6)	0.0018 (5)	0.0048 (5)	0.0021 (5)
C2	0.0127 (6)	0.0117 (6)	0.0179 (6)	0.0034 (5)	0.0052 (5)	0.0037 (5)
C9	0.0156 (6)	0.0113 (6)	0.0130 (6)	0.0003 (5)	0.0044 (5)	0.0007 (5)
C1	0.0129 (6)	0.0127 (6)	0.0169 (6)	0.0039 (5)	0.0037 (5)	0.0037 (5)
C3	0.0148 (6)	0.0158 (6)	0.0177 (6)	0.0049 (5)	0.0065 (5)	0.0045 (5)
C18	0.0151 (6)	0.0161 (6)	0.0134 (6)	0.0034 (5)	0.0031 (5)	0.0004 (5)
C23	0.0132 (6)	0.0149 (6)	0.0171 (6)	0.0049 (5)	0.0022 (5)	−0.0012 (5)
C5	0.0136 (6)	0.0117 (6)	0.0198 (7)	0.0005 (5)	0.0032 (5)	0.0031 (5)
C10	0.0179 (7)	0.0144 (6)	0.0158 (6)	0.0006 (5)	0.0025 (5)	0.0032 (5)
C24	0.0134 (6)	0.0143 (6)	0.0182 (6)	0.0051 (5)	0.0024 (5)	−0.0001 (5)
C19	0.0213 (7)	0.0182 (7)	0.0116 (6)	0.0042 (5)	0.0048 (5)	0.0042 (5)
C12	0.0157 (6)	0.0153 (6)	0.0133 (6)	−0.0003 (5)	0.0034 (5)	0.0030 (5)
C11	0.0173 (7)	0.0168 (7)	0.0169 (7)	0.0002 (5)	−0.0003 (5)	0.0051 (5)
C6	0.0156 (7)	0.0205 (7)	0.0268 (7)	0.0044 (6)	0.0062 (6)	0.0049 (6)
C26	0.0186 (7)	0.0218 (7)	0.0179 (7)	0.0061 (6)	0.0027 (5)	0.0043 (5)
C21	0.0181 (7)	0.0175 (7)	0.0185 (7)	−0.0013 (5)	0.0014 (5)	0.0030 (5)
C28	0.0170 (7)	0.0171 (7)	0.0256 (7)	0.0021 (5)	0.0002 (6)	0.0015 (6)
C14	0.0234 (8)	0.0197 (7)	0.0240 (8)	0.0009 (6)	−0.0026 (6)	0.0101 (6)
C7	0.0218 (7)	0.0309 (8)	0.0195 (7)	0.0049 (6)	0.0070 (6)	0.0109 (6)
C13	0.0292 (8)	0.0215 (7)	0.0223 (7)	−0.0047 (6)	0.0086 (6)	−0.0056 (6)
C20	0.0371 (9)	0.0300 (8)	0.0190 (7)	0.0177 (7)	0.0059 (7)	0.0050 (6)
C27	0.0367 (9)	0.0478 (10)	0.0173 (7)	0.0218 (8)	0.0071 (7)	0.0050 (7)
O3	0.0255 (5)	0.0181 (5)	0.0179 (5)	0.0032 (4)	0.0036 (4)	0.0060 (4)
O5	0.0225 (5)	0.0241 (5)	0.0230 (5)	0.0039 (4)	0.0061 (4)	0.0090 (4)

Geometric parameters (Å, º)

O2—C8	1.2467 (15)	C5—C6	1.530 (2)
O6—C22	1.2100 (16)	C10—C11	1.5026 (19)
O4—C15	1.2115 (16)	C10—C14	1.4945 (18)
O1—C1	1.2495 (15)	C24—C28	1.4887 (19)
N1—H1	0.887 (16)	C19—H19A	0.9900
N1—C4	1.4500 (16)	C19—H19B	0.9900
N1—C1	1.3395 (17)	C19—C20	1.526 (2)
N3—H3	0.875 (17)	C12—H12A	0.9900
N3—C15	1.3846 (17)	C12—H12B	0.9900
N3—C18	1.3838 (17)	C12—C13	1.523 (2)

N2—H2	0.879 (16)	C11—H11A	0.9900
N2—C8	1.3391 (17)	C11—H11B	0.9900
N2—C11	1.4491 (17)	C6—H6A	0.9800
N4—H4	0.856 (17)	C6—H6B	0.9800
N4—C22	1.3865 (17)	C6—H6C	0.9800
N4—C25	1.3848 (17)	C26—H26A	0.9900
C17—C16	1.3389 (18)	C26—H26B	0.9900
C17—C18	1.5023 (18)	C26—C27	1.523 (2)
C17—C21	1.4874 (18)	C21—H21A	0.9800
C22—C23	1.5047 (18)	C21—H21B	0.9800
C15—C16	1.5028 (18)	C21—H21C	0.9800
C16—C19	1.4899 (18)	C28—H28A	0.9800
C4—H4A	0.9900	C28—H28B	0.9800
C4—H4B	0.9900	C28—H28C	0.9800
C4—C3	1.5040 (18)	C14—H14A	0.9800
C25—C24	1.5031 (18)	C14—H14B	0.9800
C25—O5	1.2132 (16)	C14—H14C	0.9800
C8—C9	1.4871 (17)	C7—H7A	0.9800
C2—C1	1.4842 (17)	C7—H7B	0.9800
C2—C3	1.3415 (18)	C7—H7C	0.9800
C2—C5	1.4936 (18)	C13—H13A	0.9800
C9—C10	1.3380 (19)	C13—H13B	0.9800
C9—C12	1.4934 (18)	C13—H13C	0.9800
C3—C7	1.4900 (18)	C20—H20A	0.9800
C18—O3	1.2124 (16)	C20—H20B	0.9800
C23—C24	1.3419 (18)	C20—H20C	0.9800
C23—C26	1.4918 (18)	C27—H27A	0.9800
C5—H5A	0.9900	C27—H27B	0.9800
C5—H5B	0.9900	C27—H27C	0.9800

C4—N1—H1	124.0 (10)	H19A—C19—H19B	108.0
C1—N1—H1	123.9 (10)	C20—C19—H19A	109.4
C1—N1—C4	111.72 (11)	C20—C19—H19B	109.4
C15—N3—H3	123.6 (11)	C9—C12—H12A	109.4
C18—N3—H3	126.2 (11)	C9—C12—H12B	109.4
C18—N3—C15	110.15 (11)	C9—C12—C13	111.30 (11)
C8—N2—H2	122.8 (10)	H12A—C12—H12B	108.0
C8—N2—C11	111.70 (11)	C13—C12—H12A	109.4
C11—N2—H2	125.5 (10)	C13—C12—H12B	109.4
C22—N4—H4	123.8 (11)	N2—C11—C10	102.71 (11)
C25—N4—H4	125.6 (11)	N2—C11—H11A	111.2
C25—N4—C22	110.40 (11)	N2—C11—H11B	111.2
C16—C17—C18	108.26 (11)	C10—C11—H11A	111.2
C16—C17—C21	130.11 (12)	C10—C11—H11B	111.2
C21—C17—C18	121.63 (11)	H11A—C11—H11B	109.1
O6—C22—N4	126.14 (12)	C5—C6—H6A	109.5
O6—C22—C23	127.07 (12)	C5—C6—H6B	109.5
N4—C22—C23	106.79 (11)	C5—C6—H6C	109.5

O4—C15—N3	125.76 (13)	H6A—C6—H6B	109.5
O4—C15—C16	127.26 (12)	H6A—C6—H6C	109.5
N3—C15—C16	106.98 (11)	H6B—C6—H6C	109.5
C17—C16—C15	107.82 (11)	C23—C26—H26A	109.4
C17—C16—C19	130.63 (12)	C23—C26—H26B	109.4
C19—C16—C15	121.53 (11)	C23—C26—C27	111.36 (12)
N1—C4—H4A	111.2	H26A—C26—H26B	108.0
N1—C4—H4B	111.2	C27—C26—H26A	109.4
N1—C4—C3	102.76 (10)	C27—C26—H26B	109.4
H4A—C4—H4B	109.1	C17—C21—H21A	109.5
C3—C4—H4A	111.2	C17—C21—H21B	109.5
C3—C4—H4B	111.2	C17—C21—H21C	109.5
N4—C25—C24	106.64 (11)	H21A—C21—H21B	109.5
O5—C25—N4	126.34 (13)	H21A—C21—H21C	109.5
O5—C25—C24	127.01 (12)	H21B—C21—H21C	109.5
O2—C8—N2	125.99 (12)	C24—C28—H28A	109.5
O2—C8—C9	126.30 (12)	C24—C28—H28B	109.5
N2—C8—C9	107.71 (11)	C24—C28—H28C	109.5
C1—C2—C5	121.51 (11)	H28A—C28—H28B	109.5
C3—C2—C1	108.08 (11)	H28A—C28—H28C	109.5
C3—C2—C5	130.31 (12)	H28B—C28—H28C	109.5
C8—C9—C12	121.34 (11)	C10—C14—H14A	109.5
C10—C9—C8	107.89 (11)	C10—C14—H14B	109.5
C10—C9—C12	130.69 (12)	C10—C14—H14C	109.5
O1—C1—N1	125.75 (12)	H14A—C14—H14B	109.5
O1—C1—C2	126.53 (12)	H14A—C14—H14C	109.5
N1—C1—C2	107.71 (11)	H14B—C14—H14C	109.5
C2—C3—C4	109.72 (11)	C3—C7—H7A	109.5
C2—C3—C7	128.87 (13)	C3—C7—H7B	109.5
C7—C3—C4	121.41 (12)	C3—C7—H7C	109.5
N3—C18—C17	106.77 (11)	H7A—C7—H7B	109.5
O3—C18—N3	125.96 (12)	H7A—C7—H7C	109.5
O3—C18—C17	127.27 (12)	H7B—C7—H7C	109.5
C24—C23—C22	107.84 (11)	C12—C13—H13A	109.5
C24—C23—C26	131.04 (12)	C12—C13—H13B	109.5
C26—C23—C22	121.03 (12)	C12—C13—H13C	109.5
C2—C5—H5A	109.6	H13A—C13—H13B	109.5
C2—C5—H5B	109.6	H13A—C13—H13C	109.5
C2—C5—C6	110.49 (11)	H13B—C13—H13C	109.5
H5A—C5—H5B	108.1	C19—C20—H20A	109.5
C6—C5—H5A	109.6	C19—C20—H20B	109.5
C6—C5—H5B	109.6	C19—C20—H20C	109.5
C9—C10—C11	109.98 (11)	H20A—C20—H20B	109.5
C9—C10—C14	128.69 (13)	H20A—C20—H20C	109.5
C14—C10—C11	121.33 (12)	H20B—C20—H20C	109.5
C23—C24—C25	108.31 (11)	C26—C27—H27A	109.5
C23—C24—C28	130.25 (12)	C26—C27—H27B	109.5
C28—C24—C25	121.43 (12)	C26—C27—H27C	109.5

C16—C19—H19A	109.4	H27A—C27—H27B	109.5
C16—C19—H19B	109.4	H27A—C27—H27C	109.5
C16—C19—C20	110.95 (11)	H27B—C27—H27C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.89 (2)	1.97 (2)	2.8487 (15)	173 (2)
N2—H2···O1	0.88 (2)	2.05 (2)	2.9222 (15)	171 (2)
N3—H3···O1	0.88 (2)	1.97 (2)	2.8202 (15)	165 (2)
N4—H4···O2	0.86 (2)	2.03 (2)	2.8677 (15)	165 (2)