organic compounds

Polymorphic form II of 4,4′-methylenebis(benzenesulfonamide)

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In the title compound, $C_{13}H_{14}N_2O_4S_2$ (alternative names: diphenylmethane-4,4′-disulfonamide, nirexon, CRN: 535–66-0), the two benzene rings form a dihedral angle of 70.8 (1)°. There are two sets of shorter (H···O < 2.1 Å) and longer (H···O > 2.4 Å) N—H···O hydrogen bonds per sulfonamide NH_2 group, which together result in hydrogen-bonded sheets parallel (102). Adjacent sheets are connected to one another by an additional N—H···N interaction so that a three-dimensional network of hydrogen-bonded molecules is formed. The investigated polymorph is identical with the form II previously described by Kuhnert-Brandstätter & Moser [(1981). *Mikrochim. Acta*, **75**, 421–440].

Related literature

For the polymorphism of diphenylmethane-4,4′-disulfonamide, see Kuhnert-Brandstätter & Moser (1981); Kuhnert-Brandstätter & Wunsch (1969).
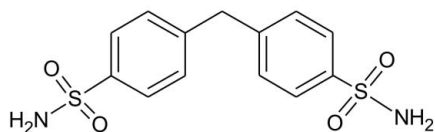
Experimental

Crystal data

$C_{13}H_{14}N_2O_4S_2$
$M_r = 326.38$
Monoclinic, $P2_1$
$a = 10.8251$ (5) Å
$b = 5.0791$ (3) Å
$c = 12.6912$ (5) Å
$\beta = 90.931$ (3)°

$V = 697.69$ (6) Å³
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.40$ mm^{-1}
$T = 120$ K
$0.25 \times 0.1 \times 0.05$ mm

Data collection

Bruker–Nonius Roper CCD camera on κ-goniostat diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
$T_{min} = 0.907$, $T_{max} = 0.980$

7877 measured reflections
2438 independent reflections
2152 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.087$
$S = 1.06$
2438 reflections
216 parameters
5 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}
Absolute structure: Flack (1983), 904 Friedel pairs
Flack parameter: −0.18 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^i	0.88 (2)	2.09 (2)	2.960 (4)	168 (4)
N1—H2···O1^{ii}	0.89 (2)	2.42 (3)	3.166 (4)	142 (3)
N1—H2···O4^{iii}	0.89 (2)	2.53 (3)	3.116 (4)	124 (3)
N2—H3···O3^{iv}	0.88 (2)	2.06 (2)	2.898 (3)	159 (3)
N2—H4···N1^v	0.88 (2)	2.50 (3)	3.182 (3)	135 (3)
N2—H4···O4^{vi}	0.88 (2)	2.50 (3)	3.149 (4)	131 (3)

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + 1$; (ii) $x, y + 1, z$; (iii) $-x + 1, y - \frac{1}{2}, -z + 1$; (iv) $-x + 2, y - \frac{1}{2}, -z$; (v) $-x + 1, y + \frac{1}{2}, -z + 1$; (vi) $x, y - 1, z$.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2209).

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supporting information

Polymorphic form II of 4,4′-methylenebis(benzenesulfonamide)

**Thomas Gelbrich, Mairi F. Haddow and Ulrich J. Griesser**

S1. Comment

The polymorphic behaviour of the title compound, a carbonic anhydrase inhibitor with diuretic effects, was described by Kuhnert-Brandstätter & Moser (1981) and Kuhnert-Brandstätter & Wunsch (1969), who identified five distinct polymorphic modifications. The commercial product contained form II (mp. 172–174 °C), which was also found to be the stable polymorph at room temperature. The identity of the crystals investigated in the present study with form II reported by Kuhnert-Brandstätter & Moser (1981) was established by thermomicroscopy and IR spectroscopy. The asymmetric unit contains a single molecule (Fig. 1). Its central plane, defined by S1, S2, C1, C11, C14, C21 and C24, forms angles of 21.8 (1)° and 78.7 (1)° with the mean planes of the two phenyl rings C11 > C16 and C21 > C26, respectively. The two sulfonamide groups are differently oriented with respect to the adjacent phenyl ring, so that the corresponding torsion angles N1—S1—C1—C24 and N2—S2—C1—C14 are 115.6 (2)° and 53.3 (2)°, respectively. Each molecule is connected to four other molecules by four short N—H⋯O bonds (H⋯O < 2.1 Å, see Table 2) so that an H-bonded sheet parallel to (102) is formed. The symmetry operation between molecules linked by these primary interactions involving one H-bond donor and one acceptor site of each sulfonamide group is a twofold screw axis. There are two additional N—H⋯O contacts (H⋯O > 2.4 Å, see Table 2) within the same plane so that all four NH hydrogen bond donor sites are employed once. These secondary N—H⋯O bonds link molecules related by a translation along [010]. The O3 and O4 sites of one sulfonyl group accept one H-bond each, while in the group O1 accepts two H-bonds. Thus, the sulfonamide groups of molecules in the hydrogen bonded sheet form two distinct chains of fused rings both propagating parallel to [010]. One chain consists of ten-membered rings with two H-bond donor and two acceptor sites (labeled ′A′ in Fig. 2), and the other is generated from 9-membered rings with two three H-bond donor and two acceptor sites (′B′). Each of the N—H⋯O sheets is linked to two neighbouring sheets by a N2—H⋯N1(-*x* + 1, *y* + 1/2, -*z* + 1) interaction (represented by arrows in Fig. 2). Thus, this crystal structure contains a three-dimensional network of N—H⋯O and N—H⋯N bonded molecules of diphenylmethane-4,4′-disulfonamide.

S2. Experimental

The crystals for this study were obtained from a commercial sample of diphenylmethane-4,4′-disulfonamide (Farbenfabriken Bayer AG, Leverkusen).

S3. Refinement

All H atoms were identified in a difference map. H atoms bonded to secondary CH$_2$ (C—H = 0.99 Å) and aromatic carbon atoms (C—H = 0.95 Å) were positioned geometrically. Hydrogen atoms attached to N were refined with restrained distances [N—H = 0.88 (12) Å]. The U_{iso} parameters of all H atoms were refined freely.
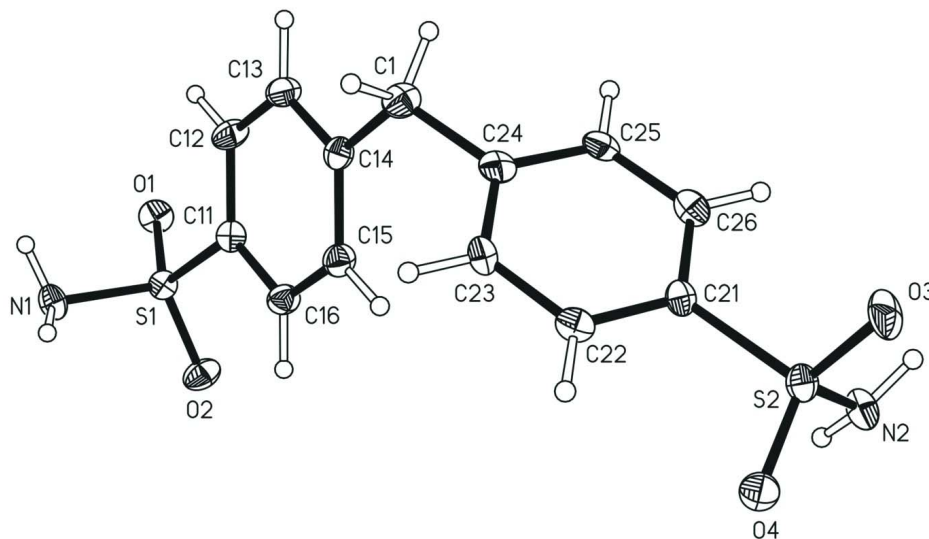
Figure 1

The molecular structure with displacement ellipsoids drawn at the 50% probability level and hydrogen atoms shown as spheres of arbitrary size.
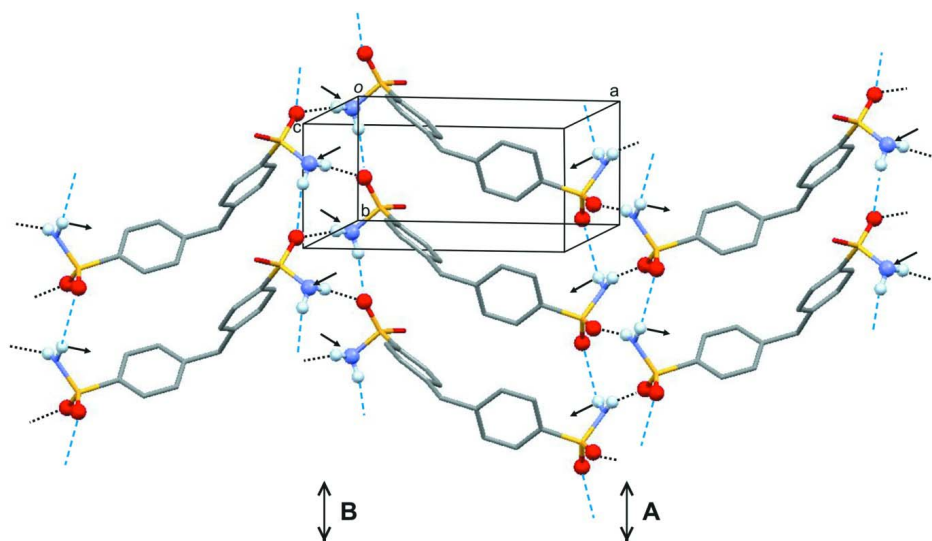
Figure 2

Portion of a single hydrogen bonded sheet parallel to (102) and generated by shorter N—H···O bonds (dotted lines) and longer N—H···O bonds (dashed lines). N—H···N bonds (arrows) connect to neighbouring sheets. O, H and N atoms directly involved in hydrogen bonds are drawn as balls.

4,4′-methylenebis(benzenesulfonamide)

Crystal data

$C_{13}H_{14}N_2O_4S_2$	$b = 5.0791\ (3)$ Å
$M_r = 326.38$	$c = 12.6912\ (5)$ Å
Monoclinic, $P2_1$	$\beta = 90.931\ (3)°$
Hall symbol: P 2yb	$V = 697.69\ (6)$ Å^3
$a = 10.8251\ (5)$ Å	$Z = 2$

$F(000) = 340$
$D_x = 1.554$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6304 reflections
$\theta = 2.9–26.0°$

$\mu = 0.40$ mm^{-1}
$T = 120$ K
Needle, colourless
$0.25 \times 0.1 \times 0.05$ mm

Data collection

Bruker–Nonius Roper CCD camera on κ-
goniostat
diffractometer
Radiation source: Bruker–Nonius FR591
rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ & ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2007)

$T_{min} = 0.907$, $T_{max} = 0.980$
7877 measured reflections
2438 independent reflections
2152 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 26.0°$, $\theta_{min} = 3.7°$
$h = -13 \rightarrow 12$
$k = -5 \rightarrow 6$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.087$
$S = 1.06$
2438 reflections
216 parameters
5 restraints
Primary atom site location: structure-invariant
direct methods
Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.182P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}
Absolute structure: Flack (1983), 904 Friedel
pairs
Absolute structure parameter: −0.18 (9)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.20189 (6)	−0.23188 (15)	0.54432 (5)	0.01593 (18)
S2	0.88754 (6)	0.73072 (17)	0.14221 (5)	0.01695 (19)
O1	0.1335 (2)	−0.4632 (4)	0.51332 (16)	0.0205 (5)
O2	0.30683 (18)	−0.2579 (6)	0.61295 (14)	0.0238 (5)
O3	0.90887 (19)	0.8314 (5)	0.03829 (15)	0.0249 (6)
O4	0.90645 (19)	0.9060 (4)	0.23016 (16)	0.0208 (5)
N1	0.1033 (3)	−0.0417 (6)	0.6023 (2)	0.0189 (6)
H1	0.035 (3)	−0.039 (10)	0.563 (3)	0.053 (13)*

H2	0.129 (3)	0.124 (4)	0.608 (3)	0.035 (11)*
N2	0.9759 (2)	0.4794 (6)	0.1575 (2)	0.0197 (6)
H3	0.994 (3)	0.410 (7)	0.0960 (18)	0.030 (10)*
H4	0.965 (3)	0.381 (7)	0.213 (2)	0.042 (12)*
C1	0.3517 (3)	0.3849 (7)	0.1577 (2)	0.0208 (7)
H1A	0.3319	0.2784	0.0943	0.024 (8)*
H1B	0.2990	0.5441	0.1550	0.028 (10)*
C11	0.2504 (3)	−0.0654 (6)	0.4304 (2)	0.0169 (7)
C12	0.1806 (3)	−0.0834 (7)	0.3372 (2)	0.0212 (7)
H12	0.1097	−0.1934	0.3335	0.021 (8)*
C13	0.2160 (3)	0.0610 (7)	0.2502 (2)	0.0200 (7)
H13	0.1696	0.0470	0.1863	0.032 (10)*
C14	0.3184 (2)	0.2261 (7)	0.2547 (2)	0.0164 (6)
C15	0.3882 (2)	0.2386 (8)	0.3479 (2)	0.0189 (6)
H15	0.4599	0.3463	0.3514	0.045 (12)*
C16	0.3538 (3)	0.0945 (7)	0.4360 (2)	0.0188 (7)
H16	0.4011	0.1058	0.4995	0.026 (9)*
C21	0.7330 (3)	0.6228 (6)	0.1479 (2)	0.0151 (6)
C22	0.6511 (2)	0.7639 (7)	0.2093 (2)	0.0174 (6)
H22	0.6786	0.9108	0.2497	0.037 (11)*
C23	0.5271 (3)	0.6854 (6)	0.2106 (2)	0.0179 (7)
H23	0.4702	0.7814	0.2520	0.021 (8)*
C24	0.4857 (3)	0.4701 (6)	0.1528 (2)	0.0170 (7)
C25	0.5703 (3)	0.3302 (7)	0.0928 (2)	0.0183 (7)
H25	0.5432	0.1810	0.0536	0.030 (10)*
C26	0.6932 (3)	0.4053 (7)	0.0892 (2)	0.0187 (7)
H26	0.7498	0.3100	0.0473	0.043 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0169 (3)	0.0134 (4)	0.0174 (3)	−0.0005 (4)	0.0005 (2)	0.0018 (4)
S2	0.0179 (4)	0.0157 (4)	0.0174 (3)	−0.0004 (4)	0.0033 (3)	0.0020 (4)
O1	0.0255 (12)	0.0093 (11)	0.0268 (12)	−0.0053 (10)	0.0004 (9)	−0.0009 (10)
O2	0.0203 (10)	0.0268 (13)	0.0241 (10)	−0.0016 (12)	−0.0057 (8)	0.0087 (13)
O3	0.0256 (12)	0.0306 (15)	0.0187 (10)	0.0016 (10)	0.0085 (8)	0.0113 (10)
O4	0.0222 (11)	0.0154 (12)	0.0249 (11)	−0.0026 (10)	0.0013 (9)	−0.0060 (10)
N1	0.0232 (15)	0.0143 (15)	0.0193 (14)	0.0003 (13)	0.0061 (11)	−0.0001 (12)
N2	0.0231 (14)	0.0191 (16)	0.0170 (14)	0.0058 (13)	0.0049 (11)	0.0032 (12)
C1	0.0209 (16)	0.0217 (18)	0.0196 (16)	−0.0019 (15)	−0.0019 (12)	0.0066 (14)
C11	0.0178 (15)	0.0145 (16)	0.0183 (14)	0.0002 (14)	0.0012 (12)	0.0014 (13)
C12	0.0173 (16)	0.0217 (19)	0.0246 (16)	−0.0055 (15)	−0.0045 (12)	0.0016 (15)
C13	0.0184 (16)	0.0229 (18)	0.0186 (15)	−0.0020 (15)	−0.0032 (12)	0.0005 (14)
C14	0.0155 (14)	0.0149 (16)	0.0189 (13)	0.0007 (15)	0.0011 (10)	0.0006 (15)
C15	0.0176 (14)	0.0204 (16)	0.0188 (13)	−0.0024 (17)	0.0009 (11)	0.0022 (17)
C16	0.0178 (16)	0.0191 (17)	0.0194 (15)	−0.0032 (14)	−0.0010 (12)	−0.0008 (13)
C21	0.0169 (15)	0.0134 (16)	0.0153 (13)	0.0005 (13)	0.0031 (11)	0.0024 (13)
C22	0.0228 (15)	0.0124 (15)	0.0169 (13)	−0.0014 (15)	−0.0009 (11)	0.0002 (16)

C23	0.0184 (15)	0.0181 (18)	0.0174 (14)	0.0015 (13)	0.0054 (12)	−0.0014 (13)
C24	0.0222 (16)	0.0168 (17)	0.0118 (14)	0.0009 (14)	−0.0020 (12)	0.0076 (13)
C25	0.0244 (16)	0.0183 (18)	0.0123 (13)	−0.0037 (13)	−0.0008 (12)	−0.0027 (12)
C26	0.0245 (16)	0.0153 (17)	0.0163 (14)	0.0028 (15)	0.0019 (12)	0.0002 (14)

Geometric parameters (Å, º)

S1—O2	1.4263 (19)	C12—C13	1.385 (4)
S1—O1	1.440 (2)	C12—H12	0.9500
S1—N1	1.624 (3)	C13—C14	1.390 (4)
S1—C11	1.762 (3)	C13—H13	0.9500
S2—O3	1.437 (2)	C14—C15	1.395 (4)
S2—O4	1.440 (2)	C15—C16	1.391 (4)
S2—N2	1.605 (3)	C15—H15	0.9500
S2—C21	1.763 (3)	C16—H16	0.9500
N1—H1	0.881 (19)	C21—C22	1.389 (4)
N1—H2	0.887 (19)	C21—C26	1.397 (4)
N2—H3	0.883 (18)	C22—C23	1.401 (4)
N2—H4	0.875 (19)	C22—H22	0.9500
C1—C24	1.516 (4)	C23—C24	1.387 (4)
C1—C14	1.520 (4)	C23—H23	0.9500
C1—H1A	0.9900	C24—C25	1.395 (4)
C1—H1B	0.9900	C25—C26	1.386 (4)
C11—C16	1.384 (4)	C25—H25	0.9500
C11—C12	1.396 (4)	C26—H26	0.9500
O2—S1—O1	119.49 (15)	C12—C13—C14	121.1 (3)
O2—S1—N1	107.52 (14)	C12—C13—H13	119.4
O1—S1—N1	105.68 (14)	C14—C13—H13	119.4
O2—S1—C11	107.49 (13)	C13—C14—C15	118.9 (3)
O1—S1—C11	109.03 (14)	C13—C14—C1	119.1 (3)
N1—S1—C11	107.02 (15)	C15—C14—C1	122.0 (3)
O3—S2—O4	117.93 (14)	C16—C15—C14	120.6 (3)
O3—S2—N2	106.86 (13)	C16—C15—H15	119.7
O4—S2—N2	108.72 (13)	C14—C15—H15	119.7
O3—S2—C21	108.36 (13)	C11—C16—C15	119.7 (3)
O4—S2—C21	106.48 (13)	C11—C16—H16	120.2
N2—S2—C21	108.18 (15)	C15—C16—H16	120.2
S1—N1—H1	108 (3)	C22—C21—C26	120.9 (3)
S1—N1—H2	114 (2)	C22—C21—S2	118.5 (2)
H1—N1—H2	107 (4)	C26—C21—S2	120.6 (2)
S2—N2—H3	111 (2)	C21—C22—C23	118.7 (3)
S2—N2—H4	118 (3)	C21—C22—H22	120.6
H3—N2—H4	121 (4)	C23—C22—H22	120.6
C24—C1—C14	115.1 (2)	C24—C23—C22	121.3 (3)
C24—C1—H1A	108.5	C24—C23—H23	119.4
C14—C1—H1A	108.5	C22—C23—H23	119.4
C24—C1—H1B	108.5	C23—C24—C25	118.8 (3)

C14—C1—H1B	108.5	C23—C24—C1	120.2 (3)
H1A—C1—H1B	107.5	C25—C24—C1	120.9 (3)
C16—C11—C12	120.5 (3)	C26—C25—C24	121.1 (3)
C16—C11—S1	119.5 (2)	C26—C25—H25	119.4
C12—C11—S1	120.0 (2)	C24—C25—H25	119.4
C13—C12—C11	119.2 (3)	C25—C26—C21	119.2 (3)
C13—C12—H12	120.4	C25—C26—H26	120.4
C11—C12—H12	120.4	C21—C26—H26	120.4

Hydrogen-bond geometry (Å, º)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1[i]	0.88 (2)	2.09 (2)	2.960 (4)	168 (4)
N1—H2$\cdots$O1[ii]	0.89 (2)	2.42 (3)	3.166 (4)	142 (3)
N1—H2$\cdots$O4[iii]	0.89 (2)	2.53 (3)	3.116 (4)	124 (3)
N2—H3$\cdots$O3[iv]	0.88 (2)	2.06 (2)	2.898 (3)	159 (3)
N2—H4$\cdots$N1[v]	0.88 (2)	2.50 (3)	3.182 (3)	135 (3)
N2—H4$\cdots$O4[vi]	0.88 (2)	2.50 (3)	3.149 (4)	131 (3)

Symmetry codes: (i) −*x*, *y*+1/2, −*z*+1; (ii) *x*, *y*+1, *z*; (iii) −*x*+1, *y*−1/2, −*z*+1; (iv) −*x*+2, *y*−1/2, −*z*; (v) −*x*+1, *y*+1/2, −*z*+1; (vi) *x*, *y*−1, *z*.