Color center creation by dipole stacking in crystals of 2-methoxy-5-nitroaniline

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This work describes the X-ray structure of orange–red crystals of 2-methoxy-5-nitroaniline, $C_7H_8N_2O_3$. The compound displays concentration-dependent UV-Vis spectra, which is attributed to dipole-induced aggregation, and light absorption arising from an intermolecular charge-transfer process that decreases in energy as the degree of aggregation increases. The crystals display π-stacking where the dipole moments align antiparallel. Stacked molecules interact with the next stack *via* hydrogen bonds, which is a state of maximum aggregation. Light absorption by charge transfer can be compared to colored inorganic semiconductors such as orange–red CdS, with a band gap of 2.0–2.5 eV.

1. Chemical context

The title compound is an inexpensive and versatile starting material with two chemically distinct nitrogen atoms that can be functionalized is a variety of ways. The molecule features *para*-oriented electron-donating and withdrawing groups as shown in the scheme, giving rise to a large dipole moment of 5.4 D (Buemi *et al.* 1979). During routine crystallization prior to its use in synthesis, we were struck by the beauty of its orange–red crystals and the ease of their formation. While dilute solutions of the compound in acetone are yellow ($\lambda_{max} = 380$ nm), more concentrated solutions exhibit a striking longer wavelength absorption, which moves further into the visible portion of the spectrum as the concentration increases (Fig. 1). These spectra are consistent with a concentration-dependent aggregation phenomenon aided by the strong dipole moment,
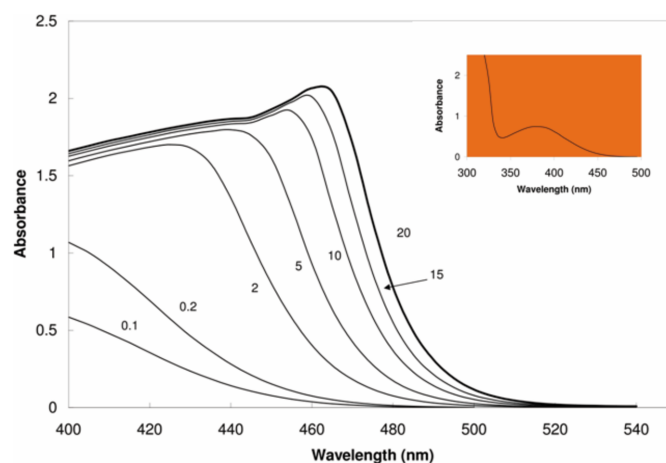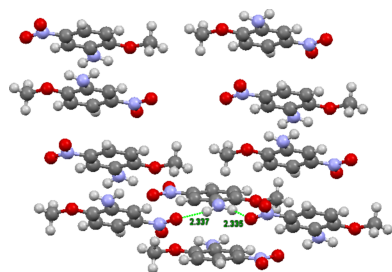

Figure 1
Concentration-dependent spectra in acetone in the visible region for 2-methoxy-5-nitroaniline (concentrations in m*M*). Inset: UV-Vis spectrum (0.1 m*M*).

which results in intermolecular charge transfer, where the electronic transition comes at lower energies as the degree of aggregation increases. Presumably, at higher concentrations, light absorption would approach 490 nm, which would result in an orange–red solution according to chromaticity diagrams (Nassau, 1983). These concentrations cannot be achieved due to solubility limitations, but solid material with no solvent molecules can be considered a state of maximum aggregation.
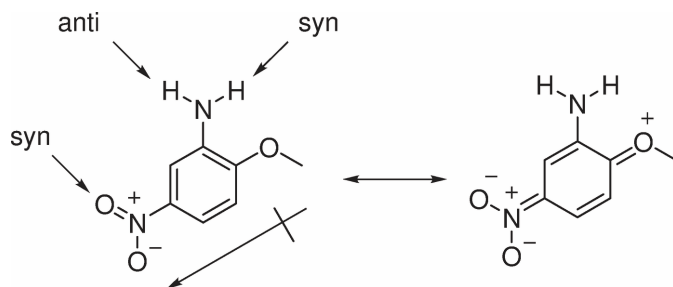
Crystals of substituted anilines comparable to 2-methoxy-5-nitroaniline have interesting non-linear optical properties (Ravikumara & Hubert Joe, 2010) and have been the subject of structure investigations (Rosli *et al.*, 2007). We undertook an X-ray structure study of the title compound to help understand the color of the crystals, and found a π-stacked face-to-face arrangement of the molecules with dipoles aligned antiparallel, which can facilitate a charge-transfer mechanism for light absorption. The color of the title compound is akin to that seen in certain inorganic semiconductors such as CdS, where a band gap of 2.0–2.5 eV gives a similar orange–red color, and is the result of charge transfer within the crystal from the valence band to the conduction band (Pal *et al.*, 1997).

2. Structural commentary

The molecular structure in Fig. 2 shows the pyramidal amino group, suggesting the amino group lone-pair electrons are not

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—H4$\cdots$O1^i	0.952 (16)	3.177 (15)	3.7473 (14)	120.2 (11)
C3—H3$\cdots$O1^i	0.944 (15)	3.039 (15)	3.6820 (14)	126.7 (11)
C3—H3$\cdots$O2^{ii}	0.944 (15)	2.646 (15)	3.3523 (14)	132.1 (11)
C6—H6$\cdots$O1^{iii}	0.958 (16)	3.006 (16)	3.7075 (14)	131.2 (11)
C6—H6$\cdots$O2^{iv}	0.958 (16)	2.527 (15)	3.3090 (14)	138.8 (12)
C6—H6$\cdots$N2^{iv}	0.958 (16)	3.130 (16)	3.9611 (14)	146.0 (12)
C7—H7A$\cdots$O2^{ii}	1.001 (17)	2.691 (17)	3.6087 (16)	152.5 (12)
C7—H7B$\cdots$O3^v	0.986 (16)	3.130 (15)	3.9801 (16)	145.2 (11)
C7—H7B$\cdots$N1^i	0.986 (16)	2.990 (16)	3.8090 (16)	141.1 (11)
N1—H1A$\cdots$O3^{vi}	0.885 (17)	2.335 (17)	3.0395 (13)	136.6 (14)
C7—H7C$\cdots$N1^{vi}	0.962 (16)	2.847 (16)	3.6953 (17)	147.6 (12)
N1—H1B$\cdots$O3^{iv}	0.869 (19)	2.337 (19)	3.1812 (13)	163.9 (15)
N1—H1B$\cdots$O2^{iv}	0.869 (19)	2.903 (18)	3.6404 (14)	143.7 (14)
N1—H1B$\cdots$N2^{iv}	0.869 (19)	2.944 (19)	3.7781 (14)	161.3 (14)

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y-\frac{1}{2}, -z-\frac{1}{2}$; (v) $-x, -y+1, -z$; (vi) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

highly conjugated with the aromatic ring, consistent with an amino group *meta* to a nitro group.

3. Supramolecular features

Key features of the crystal packing are displayed in Fig. 3. It can be seen that on a pairwise basis, the molecules stack on top of each other with almost perfect alignment of the methoxy group of one molecule and the nitro group of the next molecule, with the dipoles oriented antiparallel. Indeed, this is generally observed in crystals of molecules with non-zero dipole moments, and in fact it is an ongoing challenge to design crystals with parallel dipole moments, since these are expected to have strong non-linear optical properties (Lewis *et al.*, 2000). Fig. 3 also shows an offset of about 1.7 Å for the next pair of stacked molecules. The stacked columns are connected by hydrogen bonds with lengths of 2.34 (2) Å (Table 1). Interestingly, these inter-stack hydrogen bonds connect both *syn* and *anti* amino group hydrogen atoms on
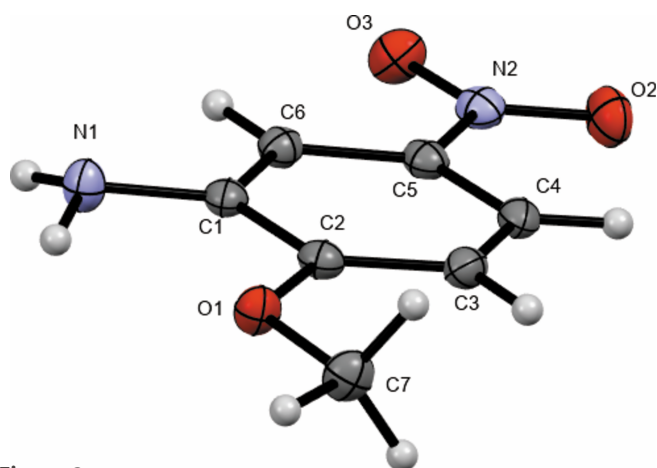

Figure 2
Molecular structure of 2-methoxy-5-nitroaniline showing the pyramidal amino group. Atoms are displayed as ellipsoids at the 50% probability displacement level.
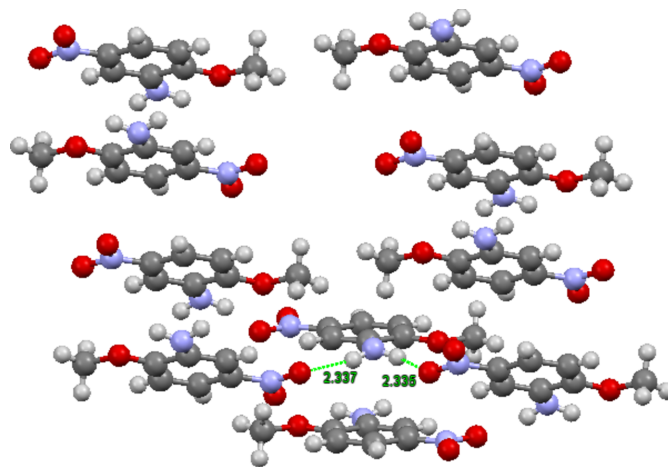

Figure 3
Stacked molecules of the title compound showing antiparallel aligned dipoles and hydrogen bonding from the amino hydrogen atoms to *syn* nitro oxygen atoms.

one stack to only the *syn* oxygen atoms of the nitro group on a different stack (the *anti* nitro oxygen atoms are not involved in hydrogen bonds). In order for this to be true, the stacks that bear nitro group oxygen atom hydrogen-bond acceptors have to be parallel, and the *syn* acceptors are flipped with respect to each other. The angle between the planes defining the two stacks is 33.6 (7)°. It is hypothesized that the observed orange–red color of the crystals arises from intermolecular charge transfer, amounting to a color center and colored semiconductor-like behavior.

4. Database survey

Related nitro anilines such as 4-methoxy-2-nitroaniline have been subjected to X-ray structure analysis (Rosli *et al.*, 2007), which shows a near planar amino group (the amino and nitro groups are *ortho* to each other and are therefore conjugated) and a slightly shorter N—H⋯O hydrogen bond of 2.20 Å. A neutron diffraction study found a slightly pyramidal amino group in 2-methyl-4-nitroaniline (Whitten *et al.*, 2006). The compound 2-bromo-4-nitroaniline has intermolecular hydrogen bonding almost identical to that reported here (Arshad *et al.*, 2009).

5. Synthesis and crystallization

2-Methoxy-5-nitroaniline was obtained from Aldrich and recrystallized from methanol. UV-VIS spectra were collected on a Perkin–Elmer Lambda 3A spectrophotometer. Spectra were collected using a path length of 1.0 cm in acetone solution. Images of molecular structures were manipulated using *Mercury* (Macrae *et al.*, 2020).

6. Refinement

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

Acknowledgements

References

Agilent (2014). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_8N_2O_3$
M_r	168.15
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	7.14981 (11), 9.79512 (11), 10.74206 (14)
β (°)	96.9437 (14)
V (Å^3)	746.78 (2)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.01
Crystal size (mm)	$0.5 \times 0.4 \times 0.2$
Data collection	
Diffractometer	Xcalibur, Onyx, Ultra
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.827, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13822, 1543, 1398
R_{int}	0.049
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.630
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.097, 1.06
No. of reflections	1543
No. of parameters	141
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.25, −0.17

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS* (Sheldrick, 2008), *SHELXL2013/4* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

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Jonathan Filley

Computing details

2-Methoxy-5-nitroaniline

Crystal data

$C_7H_8N_2O_3$	$F(000) = 352$
$M_r = 168.15$	$D_x = 1.496$ Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$a = 7.14981$ (11) Å	Cell parameters from 7580 reflections
$b = 9.79512$ (11) Å	$\theta = 4.1–75.9°$
$c = 10.74206$ (14) Å	$\mu = 1.01$ mm^{-1}
$\beta = 96.9437$ (14)°	$T = 100$ K
$V = 746.78$ (2) Å^3	Block, clear dark orange
$Z = 4$	$0.5 \times 0.4 \times 0.2$ mm

Data collection

Xcalibur, Onyx, Ultra diffractometer	$T_{min} = 0.827$, $T_{max} = 1.000$
Radiation source: sealed X-ray tube, Enhance Ultra (Cu) X-ray Source	13822 measured reflections
	1543 independent reflections
Mirror monochromator	1398 reflections with $I > 2\sigma(I)$
Detector resolution: 8.2603 pixels mm^{-1}	$R_{int} = 0.049$
ω scans	$\theta_{max} = 76.1°$, $\theta_{min} = 7.1°$
Absorption correction: multi-scan (CrysAlisPro; Agilent, 2014)	$h = -8 \rightarrow 8$
	$k = -12 \rightarrow 12$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.097$	All H-atom parameters refined
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.2402P]$
1543 reflections	where $P = (F_o^2 + 2F_c^2)/3$
141 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.25$ e Å^{-3}
	$\Delta\rho_{min} = -0.16$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.43312 (12)	0.35947 (8)	0.24323 (7)	0.0204 (2)
O3	0.09878 (13)	0.51541 (9)	−0.30006 (8)	0.0259 (2)
O2	0.05943 (13)	0.70793 (9)	−0.20810 (9)	0.0278 (2)
C3	0.28683 (16)	0.55666 (12)	0.13260 (11)	0.0192 (3)
N2	0.11198 (14)	0.58793 (10)	−0.20487 (9)	0.0201 (2)
N1	0.38353 (15)	0.20274 (10)	0.04027 (10)	0.0212 (2)
C5	0.19259 (16)	0.53005 (11)	−0.08607 (10)	0.0178 (3)
C1	0.32888 (16)	0.33783 (11)	0.02968 (11)	0.0172 (3)
C6	0.24983 (16)	0.39389 (12)	−0.08308 (10)	0.0177 (3)
C2	0.34803 (16)	0.42203 (12)	0.13800 (10)	0.0174 (3)
C4	0.20887 (16)	0.61213 (12)	0.01915 (11)	0.0190 (3)
C7	0.45834 (19)	0.43980 (13)	0.35597 (11)	0.0231 (3)
H4	0.167 (2)	0.7045 (16)	0.0136 (14)	0.025 (4)*
H3	0.301 (2)	0.6112 (15)	0.2055 (14)	0.022 (3)*
H6	0.236 (2)	0.3386 (16)	−0.1572 (15)	0.024 (4)*
H7A	0.532 (2)	0.5240 (17)	0.3417 (14)	0.032 (4)*
H7B	0.335 (2)	0.4632 (16)	0.3830 (13)	0.027 (4)*
H1A	0.459 (2)	0.1820 (16)	0.1091 (16)	0.027 (4)*
H7C	0.527 (2)	0.3821 (16)	0.4180 (14)	0.027 (4)*
H1B	0.407 (2)	0.1628 (18)	−0.0284 (17)	0.035 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0242 (4)	0.0200 (4)	0.0163 (4)	0.0008 (3)	0.0000 (3)	−0.0008 (3)
O3	0.0314 (5)	0.0261 (5)	0.0197 (4)	−0.0031 (4)	0.0004 (3)	0.0019 (3)
O2	0.0309 (5)	0.0211 (4)	0.0317 (5)	0.0056 (4)	0.0046 (4)	0.0078 (4)
C3	0.0174 (6)	0.0190 (6)	0.0215 (6)	−0.0021 (4)	0.0036 (4)	−0.0039 (4)
N2	0.0175 (5)	0.0207 (5)	0.0225 (5)	−0.0020 (4)	0.0037 (4)	0.0045 (4)
N1	0.0264 (6)	0.0183 (5)	0.0185 (5)	0.0029 (4)	0.0012 (4)	−0.0010 (4)
C5	0.0142 (5)	0.0196 (6)	0.0199 (6)	−0.0012 (4)	0.0034 (4)	0.0029 (4)
C1	0.0144 (5)	0.0174 (5)	0.0202 (5)	−0.0017 (4)	0.0042 (4)	−0.0003 (4)
C6	0.0165 (6)	0.0191 (5)	0.0180 (5)	−0.0016 (4)	0.0040 (4)	−0.0015 (4)
C2	0.0146 (6)	0.0199 (6)	0.0179 (5)	−0.0014 (4)	0.0025 (4)	0.0013 (4)
C4	0.0149 (6)	0.0165 (5)	0.0263 (6)	0.0001 (4)	0.0050 (4)	0.0006 (4)
C7	0.0265 (7)	0.0249 (6)	0.0176 (6)	−0.0007 (5)	0.0010 (5)	−0.0023 (5)

Geometric parameters (Å, º)

O1—C2	1.3627 (14)	N1—H1B	0.869 (19)
O1—C7	1.4373 (14)	C5—C6	1.3943 (16)
O3—N2	1.2393 (13)	C5—C4	1.3804 (16)
O2—N2	1.2332 (13)	C1—C6	1.3866 (16)
C3—C2	1.3884 (16)	C1—C2	1.4193 (16)
C3—C4	1.3881 (16)	C6—H6	0.958 (16)

C3—H3	0.944 (15)	C4—H4	0.952 (16)
N2—C5	1.4506 (14)	C7—H7A	1.001 (17)
N1—C1	1.3805 (15)	C7—H7B	0.986 (16)
N1—H1A	0.885 (17)	C7—H7C	0.962 (16)
C2—O1—C7	116.79 (9)	C5—C6—H6	121.4 (9)
C2—C3—H3	120.1 (9)	C1—C6—C5	119.10 (10)
C4—C3—C2	119.97 (10)	C1—C6—H6	119.5 (9)
C4—C3—H3	119.9 (9)	O1—C2—C3	124.65 (10)
O3—N2—C5	118.97 (9)	O1—C2—C1	114.07 (10)
O2—N2—O3	122.04 (10)	C3—C2—C1	121.26 (10)
O2—N2—C5	118.99 (10)	C3—C4—H4	121.1 (9)
C1—N1—H1A	115.3 (10)	C5—C4—C3	118.43 (10)
C1—N1—H1B	116.3 (11)	C5—C4—H4	120.4 (9)
H1A—N1—H1B	116.4 (15)	O1—C7—H7A	109.7 (9)
C6—C5—N2	118.58 (10)	O1—C7—H7B	110.4 (9)
C4—C5—N2	118.54 (10)	O1—C7—H7C	105.3 (9)
C4—C5—C6	122.87 (11)	H7A—C7—H7B	111.0 (13)
N1—C1—C6	122.20 (10)	H7A—C7—H7C	110.9 (13)
N1—C1—C2	119.42 (10)	H7B—C7—H7C	109.3 (12)
C6—C1—C2	118.35 (10)		
O3—N2—C5—C6	−0.95 (16)	C6—C1—C2—O1	−177.80 (9)
O3—N2—C5—C4	179.20 (10)	C6—C1—C2—C3	1.01 (17)
O2—N2—C5—C6	179.34 (10)	C2—C3—C4—C5	0.67 (17)
O2—N2—C5—C4	−0.51 (16)	C2—C1—C6—C5	0.09 (17)
N2—C5—C6—C1	179.34 (9)	C4—C3—C2—O1	177.28 (10)
N2—C5—C4—C3	−179.72 (10)	C4—C3—C2—C1	−1.41 (17)
N1—C1—C6—C5	178.05 (10)	C4—C5—C6—C1	−0.82 (18)
N1—C1—C2—O1	4.18 (15)	C7—O1—C2—C3	0.66 (16)
N1—C1—C2—C3	−177.01 (10)	C7—O1—C2—C1	179.43 (9)
C6—C5—C4—C3	0.44 (18)		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O1[i]	0.952 (16)	3.177 (15)	3.7473 (14)	120.2 (11)
C3—H3···O1[i]	0.944 (15)	3.039 (15)	3.6820 (14)	126.7 (11)
C3—H3···O2[ii]	0.944 (15)	2.646 (15)	3.3523 (14)	132.1 (11)
C6—H6···O1[iii]	0.958 (16)	3.006 (16)	3.7075 (14)	131.2 (11)
C6—H6···O2[iv]	0.958 (16)	2.527 (15)	3.3090 (14)	138.8 (12)
C6—H6···N2[iv]	0.958 (16)	3.130 (16)	3.9611 (14)	146.0 (12)
C7—H7A···O2[ii]	1.001 (17)	2.691 (17)	3.6087 (16)	152.5 (12)
C7—H7B···O3[v]	0.986 (16)	3.130 (15)	3.9801 (16)	145.2 (11)
C7—H7B···N1[i]	0.986 (16)	2.990 (16)	3.8090 (16)	141.1 (11)
N1—H1A···O3[vi]	0.885 (17)	2.335 (17)	3.0395 (13)	136.6 (14)
C7—H7C···N1[vi]	0.962 (16)	2.847 (16)	3.6953 (17)	147.6 (12)
N1—H1B···O3[iv]	0.869 (19)	2.337 (19)	3.1812 (13)	163.9 (15)

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Symmetry codes: (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $x+1/2, -y+3/2, z+1/2$; (iii) $x-1/2, -y+1/2, z-1/2$; (iv) $-x+1/2, y-1/2, -z-1/2$; (v) $-x, -y+1, -z$; (vi) $x+1/2, -y+1/2, z+1/2$.