

The Crystal Structure of the δ -Form of 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (δ -HMX)

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The crystal structure of the title compound, $C_4H_8N_8O_8$, has been determined by direct methods from counter intensities. The crystals are hexagonal, space group $P6_1$ ($P6_5$), with $a = 7.711$ (2), $c = 32.553$ (6) Å, and $Z = 6$. The final R was 0.115 for 1126 observed reflexions. The four C atoms of the eight-membered ring are planar and the molecule has approximate twofold symmetry about an axis perpendicular to this plane through the centre of the ring. The shape of the molecule is similar to that of the α -polymorph which has crystallographic twofold symmetry.

Introduction

The explosive 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) has four distinct polymorphic forms (α , β , γ and δ) and crystallographic and optical data have been reported by Small (1947), Cady, Larson & Cromer (1963) and McCrone (1950). The crystal structure of the room-temperature-stable β -HMX was determined independently by Small (1947) and Eiland & Pepinsky (1955) by X-ray diffraction and reinvestigated by Choi & Boutin (1970) by neutron diffraction. The α -HMX crystal structure, which was reported to be stable in the temperature range 103–162°C by Cady & Smith (1961), was solved by Cady *et al.* (1963). No structure determination of the γ - and δ -HMX polymorphs has been reported. The conformations of the α - and β -HMX molecules are different; α -HMX has crystallographic twofold symmetry whereas β -HMX has a centre of symmetry. It is of interest to compare the packing of the three structures and the shapes of the molecules.

Experimental

The δ -polymorph is the high-temperature-stable form and is reported to be stable from 160°C up to the melting point (Cady & Smith, 1961). Several methods were used to prepare single crystals. Large crystals were grown by refluxing β -HMX in cyclohexanone at 156°C for 30 min and from a slurry of β -HMX in tris-(β -chloroethyl)phosphate at 163°C. The crystals were filtered from the hot solutions and dried, but transformed to β -HMX within approximately 12 h. Stable crystals were prepared by sublimation at approximately 200°C under vacuum but were too

small to be used for X-ray measurements. Crystals grown by this method have been kept for more than a year without transforming. The crystals

Table 2. Observed and calculated structure amplitudes $\times 10^2$

h	k	l	Observed	Calculated
0	0	0	100	100
0	0	1	100	100
0	0	2	100	100
0	0	3	100	100
0	0	4	100	100
0	0	5	100	100
0	0	6	100	100
0	0	7	100	100
0	0	8	100	100
0	0	9	100	100
0	0	10	100	100
0	0	11	100	100
0	0	12	100	100
0	0	13	100	100
0	0	14	100	100
0	0	15	100	100
0	0	16	100	100
0	0	17	100	100
0	0	18	100	100
0	0	19	100	100
0	0	20	100	100
0	0	21	100	100
0	0	22	100	100
0	0	23	100	100
0	0	24	100	100
0	0	25	100	100
0	0	26	100	100
0	0	27	100	100
0	0	28	100	100
0	0	29	100	100
0	0	30	100	100
0	0	31	100	100
0	0	32	100	100
0	0	33	100	100
0	0	34	100	100
0	0	35	100	100
0	0	36	100	100
0	0	37	100	100
0	0	38	100	100
0	0	39	100	100
0	0	40	100	100
0	0	41	100	100
0	0	42	100	100
0	0	43	100	100
0	0	44	100	100
0	0	45	100	100
0	0	46	100	100
0	0	47	100	100
0	0	48	100	100
0	0	49	100	100
0	0	50	100	100
0	0	51	100	100
0	0	52	100	100
0	0	53	100	100
0	0	54	100	100
0	0	55	100	100
0	0	56	100	100
0	0	57	100	100
0	0	58	100	100
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0	0	60	100	100
0	0	61	100	100
0	0	62	100	100
0	0	63	100	100
0	0	64	100	100
0	0	65	100	100
0	0	66	100	100
0	0	67	100	100
0	0	68	100	100
0	0	69	100	100
0	0	70	100	100
0	0	71	100	100
0	0	72	100	100
0	0	73	100	100
0	0	74	100	100
0	0	75	100	100
0	0	76	100	100
0	0	77	100	100
0	0	78	100	100
0	0	79	100	100
0	0	80	100	100
0	0	81	100	100
0	0	82	100	100
0	0	83	100	100
0	0	84	100	100
0	0	85	100	100
0	0	86	100	100
0	0	87	100	100
0	0	88	100	100
0	0	89	100	100
0	0	90	100	100
0	0	91	100	100
0	0	92	100	100
0	0	93	100	100
0	0	94	100	100
0	0	95	100	100
0	0	96	100	100
0	0	97	100	100
0	0	98	100	100
0	0	99	100	100
0	0	100	100	100

Table 1. Crystal data

Chemical formula $C_4H_8N_8O_8$
 Hexagonal, space group $P6_1$, or $P6_5$,
 $a = 7.711$ (2) Å
 $c = 32.553$ (6)
 $V = 1676.3$ Å³
 $Z = 6$
 $D_{obs} = 1.58$ g cm⁻³
 $D_{calc} = 1.86$

eventually used were grown from cyclohexanone, filtered off quickly and stored under vacuum at a temperature of 166°C for several days. In this way the stability of the crystals at room temperature was increased and transformation occurred after 3 or 4 days. A method for stabilizing δ -HMX has been reported (Selig, 1969), in which crystals grown from *N,N*-dimethyl-*p*-toluidine were stable for many months.

Oscillation and Weissenberg photographs showed the crystals to be hexagonal and the systematic absences ($00l$ for $l \neq 6n$) indicated space groups $P6_1$, $P6_5$, $P6_122$ or $P6_222$. A zero-layer Weissenberg photograph taken for a crystal set to rotate about *c* appeared to have mirror symmetry about *a** and the space group was assumed to be $P6_222$, or the enantiomorphic $P6_522$. Difficulty in solving the crystal structure later cast doubt on the space group and a closer examination showed the space group to be $P6_1$ or the enantiomorphic $P6_5$. Cell dimensions were determined from a least-squares fit to a number of interplanar spacings measured on a three-circle diffractometer (Small & Travers, 1961) with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Measurement of the density was made by flotation. The crystal data are shown in Table 1.

The crystal used for the collection of intensities was cut in half and approximately two-thirds of the intensities (assuming space group $P6_122$) were measured before the crystal began to transform to β -HMX. The remaining intensities were measured on the other portion of the crystal which meanwhile had been stored at a temperature of 166°C. When the space group was decided to be $P6_1(P6_5)$ the remaining intensities were collected on another crystal. A total of 1252 reflexions were measured [of which 126 were unobserved, $I < \sigma(I)$] with copper radiation out to $\sin \theta/\lambda = 0.642 \text{ \AA}^{-1}$.

Determination and refinement of the structure

Corrections were applied for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods (assuming space group $P6_1$) with a September 1972 version of the program *MULTAN* (Germain, Main & Woolfson, 1971). 233 reflexions

Table 3. Fractional atomic coordinates

The values of the atomic coordinates are multiplied by 10^4 for the heavy atoms and by 10^3 for the hydrogen atoms.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	5089 (17)	8598 (18)	0 (6)
C(2)	2888 (19)	10019 (17)	218 (7)
C(3)	2546 (17)	5295 (16)	344 (7)
C(4)	407 (16)	6755 (16)	548 (6)
N(1)	6538 (19)	12227 (15)	122 (8)
N(2)	4559 (13)	7075 (13)	321 (6)
N(3)	1309 (13)	5481 (13)	654 (6)
N(4)	5923 (17)	7263 (19)	607 (7)
N(5)	1975 (14)	8878 (14)	585 (6)
N(6)	2534 (16)	9618 (15)	967 (6)
N(7)	366 (18)	3995 (17)	938 (6)
N(8)	4905 (14)	10290 (13)	137 (6)
O(1)	6204 (17)	13564 (15)	190 (—)
O(2)	5437 (18)	6038 (18)	879 (6)
O(3)	1046 (16)	2853 (15)	998 (6)
O(4)	4023 (16)	11321 (15)	985 (6)
O(5)	−924 (16)	3955 (18)	1157 (6)
O(6)	1708 (17)	8670 (16)	1264 (6)
O(7)	8154 (15)	12376 (15)	40 (7)
O(8)	7625 (15)	8753 (18)	556 (7)
H(1)	651	910	−9
H(2)	430	820	−29
H(3)	310	1130	35
H(4)	199	928	−2
H(5)	180	500	4
H(6)	270	411	41
H(7)	−10	650	25
H(8)	−20	680	83

Table 4. Thermal vibrational parameters

The U_{ij} values are multiplied by 10^4 . The temperature factor equation has the form

$$\exp \{ -2\pi^2 (U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl) \}.$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	295 (58)	411 (63)	534 (79)	115 (50)	99 (51)	−8 (57)
C(2)	420 (66)	322 (58)	626 (80)	193 (53)	−185 (57)	−86 (54)
C(3)	319 (58)	215 (50)	749 (87)	70 (45)	162 (58)	−69 (53)
C(4)	283 (54)	237 (50)	652 (75)	123 (45)	−58 (50)	−126 (48)
N(1)	523 (81)	168 (52)	1319 (131)	−83 (50)	−279 (84)	−50 (67)
N(2)	308 (45)	374 (48)	352 (43)	190 (40)	−27 (37)	41 (38)
N(3)	331 (44)	306 (47)	465 (53)	212 (39)	79 (40)	72 (40)
N(4)	480 (63)	597 (74)	693 (70)	363 (60)	−60 (60)	−18 (62)
N(5)	366 (48)	284 (45)	486 (54)	189 (40)	−124 (44)	−100 (40)
N(6)	495 (65)	368 (56)	719 (81)	283 (50)	−102 (60)	−122 (56)
N(7)	614 (71)	494 (64)	436 (55)	274 (56)	103 (54)	180 (52)
N(8)	258 (45)	125 (41)	884 (80)	−25 (35)	38 (50)	−24 (45)
O(1)	690 (84)	268 (53)	1840 (153)	51 (49)	−284 (90)	−127 (72)
O(2)	878 (82)	728 (74)	815 (79)	539 (67)	−108 (63)	172 (63)
O(3)	675 (72)	506 (59)	1127 (98)	331 (57)	66 (66)	330 (64)
O(4)	682 (69)	407 (52)	1208 (99)	249 (50)	−390 (68)	−432 (60)
O(5)	645 (69)	928 (86)	920 (84)	455 (67)	580 (67)	627 (70)
O(6)	899 (79)	682 (70)	479 (55)	490 (65)	−77 (57)	−57 (53)
O(7)	267 (54)	413 (58)	1915 (155)	−121 (44)	−99 (70)	−54 (77)
O(8)	359 (53)	680 (69)	1781 (141)	234 (53)	−455 (73)	−372 (86)

with $E > 1.30$ were used, producing 16 sets of phases, all with low ABSFOM figures of merit (0.6181–0.9209). The correct structure had the fourth-highest value of ABSFOM (0.8809) but the second lowest value of RESID and the highest value of COMBINED FOM. 17 of the 20 non-hydrogen atoms were located on the E map and the remaining 3 atoms were found after further examination in the expected positions on the map.

R for the trial structure was 0.33 and least-squares refinement of the atomic positions and anisotropic temperature factors with *CRYLSQ* of the X-RAY System

reduced R to 0.142. The separate refinement of scale factors for each crystal used reduced R to 0.125 and a difference synthesis located the hydrogen atoms. The latter were included in the model with U_{ij} values of the atoms to which they are bonded and the C, N and O atom parameters refined for two cycles of *CRYLSQ*. The positional parameters of the H atoms were not refined. The final R was 0.115 for the observed reflexions and the maximum shift to error of the heavy atoms on the last cycle of refinement was 0.24. Unit weights were used, and scattering factors were taken from *International Tables for X-ray Crystallography*

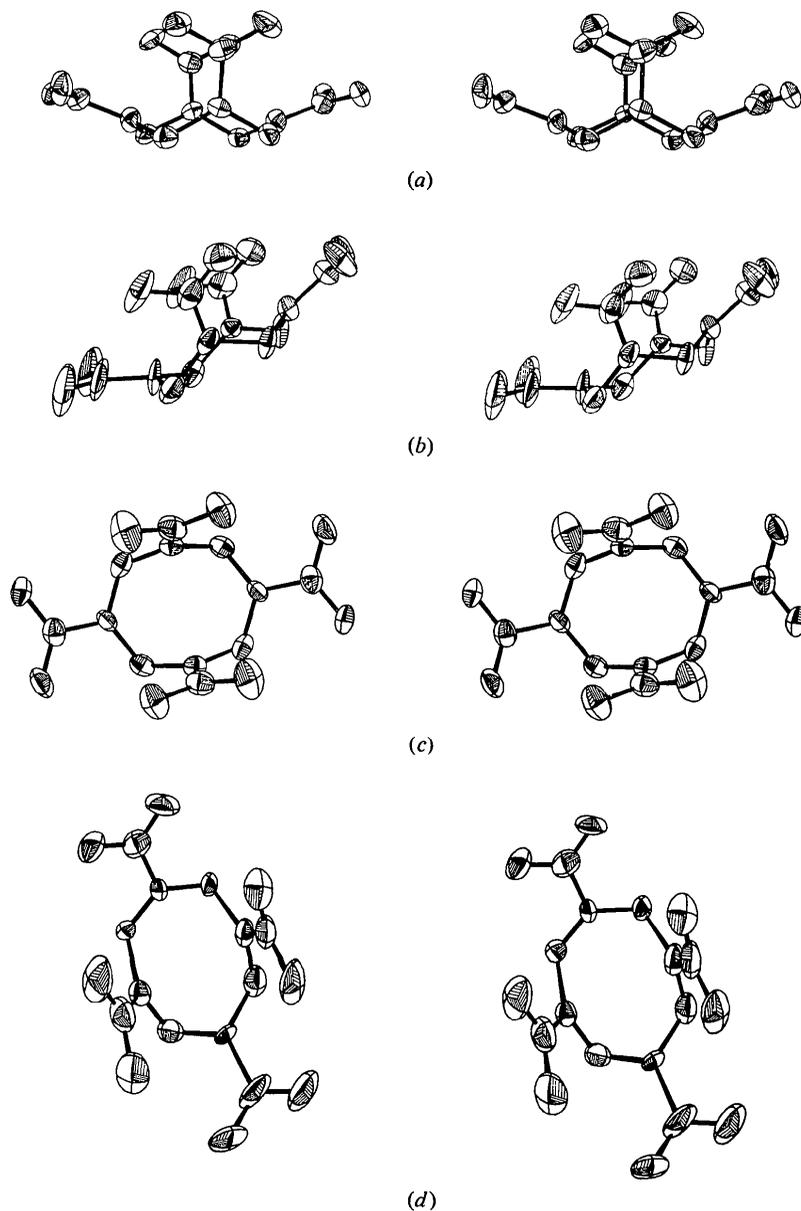


Fig. 1. Stereoscopic views of α -HMX and δ -HMX drawn by *ORTEP* (Johnson, 1965), showing thermal ellipsoids with 50% probability. (a) α -HMX viewed from the side. (b) δ -HMX viewed from the side. (c) α -HMX viewed from above. (d) δ -HMX viewed from above.

(1962). The observed and calculated structure amplitudes are shown in Table 2 and the final positional and thermal parameters in Tables 3 and 4.

Discussion of the crystal structure

Bond lengths and angles are given in Tables 5 and 6 and are comparable with those of α - and β -HMX. The shape of the molecule is similar to that of α -HMX. Fig. 1 shows views of the α - and δ -molecules for comparison. The nitramine groups ($C_2.N.NO_2$) are approximately planar and the deviations of atoms from the least-squares planes are listed in Table 7. The largest deviation of 0.319 Å [for atom C(3)] is intermediate between the largest deviation of 0.200 Å for α -HMX and 0.459 Å for β -HMX. The four carbon atoms of the eight-membered ring are almost exactly coplanar (Table 7); the figures in parentheses are the deviations for α -HMX. The δ -HMX molecule has approximate twofold symmetry about an axis through

the centre of the molecule perpendicular to the plane through the carbon atoms of the ring, whilst α -HMX has crystallographic twofold symmetry.

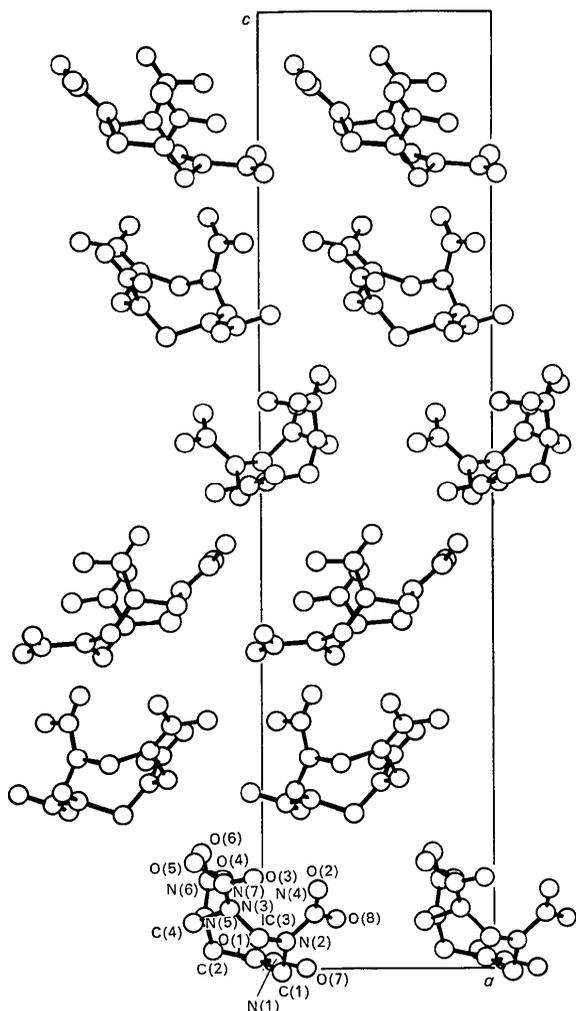


Fig. 2. Projection of the crystal structure.

Table 5. Bond distances (Å)

C(1)–N(2)	1.470 (23)	N(6)–O(4)	1.240 (12)
C(1)–N(8)	1.451 (21)	N(6)–O(6)	1.187 (23)
N(2)–C(3)	1.472 (12)	C(2)–N(8)	1.485 (19)
N(2)–N(4)	1.355 (23)	N(8)–N(1)	1.392 (12)
N(4)–O(2)	1.210 (25)	N(1)–O(1)	1.201 (21)
N(4)–O(8)	1.250 (14)	N(1)–O(7)	1.223 (21)
C(3)–N(3)	1.445 (24)	C(1)–H(1)	1.01
N(3)–C(4)	1.500 (20)	C(1)–H(2)	1.08
N(3)–N(7)	1.363 (20)	C(2)–H(3)	1.01
N(7)–O(3)	1.245 (22)	C(2)–H(4)	1.00
N(7)–O(5)	1.212 (23)	C(3)–H(5)	1.10
C(4)–N(5)	1.475 (12)	C(3)–H(6)	1.00
N(5)–C(2)	1.442 (25)	C(4)–H(7)	1.03
N(5)–N(6)	1.346 (25)	C(4)–H(8)	1.04

Table 6. Bond angles (°)

N(2)–C(1)–N(8)	112.8 (1.6)	N(1)–N(8)–C(2)	118.6 (1.2)
C(1)–N(2)–C(3)	121.5 (1.4)	O(1)–N(1)–N(8)	116.6 (1.4)
C(1)–N(2)–N(4)	120.8 (0.9)	O(1)–N(1)–O(7)	127.3 (1.0)
C(3)–N(2)–N(4)	117.8 (1.4)	N(8)–N(1)–O(7)	116.2 (1.3)
N(2)–N(4)–O(2)	119.9 (1.1)	N(2)–C(1)–H(1)	109
N(2)–N(4)–O(8)	114.2 (1.7)	N(2)–C(1)–H(2)	120
O(2)–N(4)–O(8)	126.0 (1.8)	N(8)–C(1)–H(1)	109
N(2)–C(3)–N(3)	112.5 (1.3)	N(8)–C(1)–H(2)	103
C(3)–N(3)–C(4)	116.6 (1.5)	H(1)–C(1)–H(2)	102
C(3)–N(3)–N(7)	119.4 (1.2)	N(5)–C(2)–H(3)	92
C(4)–N(3)–N(7)	118.7 (1.3)	N(5)–C(2)–H(4)	108
N(3)–N(7)–O(3)	117.7 (1.5)	N(8)–C(2)–H(3)	107
N(3)–N(7)–O(5)	120.3 (1.5)	N(8)–C(2)–H(4)	109
O(3)–N(7)–O(5)	121.3 (1.7)	H(3)–C(2)–H(4)	128
N(3)–C(4)–N(5)	108.5 (1.0)	N(2)–C(3)–H(5)	110
C(2)–N(5)–C(4)	119.3 (1.5)	N(2)–C(3)–H(6)	108
C(2)–N(5)–N(6)	123.5 (1.0)	N(3)–C(3)–H(5)	110
C(4)–N(5)–N(6)	117.2 (1.4)	N(3)–C(3)–H(6)	109
N(5)–N(6)–O(4)	115.1 (1.6)	H(5)–C(3)–H(6)	107
N(5)–N(6)–O(6)	122.1 (1.1)	N(3)–C(4)–H(7)	111
O(4)–N(6)–O(6)	122.7 (1.9)	N(3)–C(4)–H(8)	100
N(5)–C(2)–N(8)	113.0 (1.5)	N(5)–C(4)–H(7)	108
C(1)–N(8)–N(1)	120.8 (1.3)	N(5)–C(4)–H(8)	91
C(1)–N(8)–C(2)	119.6 (0.8)	H(7)–C(4)–H(8)	135

Table 7. Deviations of atoms from least-squares planes

The equations of the planes are referred to orthogonal axes a, b', c .

(a) Plane through atoms N(5), N(6), O(4) and O(6)

$$0.9232x - 0.3883y + 0.0286z = -3.9766$$

N(5)	0.004 Å
N(6)	-0.015
O(4)	0.005
O(6)	0.005
C(2)	-0.077
C(4)	0.184

(b) Plane through atoms N(1), N(8), O(1) and O(7)

$$0.2223x - 0.0510y + 0.9737z = 0.0415$$

N(1)	0.001 Å
N(8)	0.000
O(1)	0.000
O(7)	0.000
C(1)	-0.199
C(2)	-0.057

Table 7 (*cont.*)

(c) Plane through atoms N(2), N(4), O(2) and O(8)

$$-0.6111x + 0.5477y + 0.5714z = 2.7047$$

N(2)	0.000 Å
N(4)	0.001
O(2)	0.000
O(8)	0.000
C(1)	0.068
C(3)	-0.080

(d) Plane through atoms N(3), N(7), O(3) and O(5)

$$0.4115x + 0.6168y + 0.6710z = 3.2191$$

N(3)	0.013 Å
N(7)	-0.043
O(3)	0.015
O(5)	0.015
C(3)	-0.319
C(4)	-0.183

(e) Plane through atoms C(1), C(2), C(3) and C(4)

$$0.3992x + 0.3096y + 0.8630z = 2.0249$$

C(1)	-0.004 (0.041) Å	N(7)	0.933 (0.854) Å
C(2)	0.004 (-0.041)	N(8)	0.412 (0.390)
C(3)	0.004 (-0.041)	O(1)	1.135 (1.057)
C(4)	-0.005 (0.041)	O(2)	2.437 (2.488)
N(1)	0.976 (0.854)	O(3)	1.251 (1.057)
N(2)	0.655 (0.653)	O(4)	2.579 (2.488)
N(3)	0.505 (0.390)	O(5)	1.149 (1.054)
N(4)	1.887 (1.971)	O(6)	2.509 (2.567)
N(5)	0.694 (0.653)	O(7)	1.250 (1.054)
N(6)	1.979 (1.971)	O(8)	2.346 (2.567)

Fig. 2 shows a projection of the structure on the *ac* plane. Intermolecular distances less than 3.30 Å between heavy atoms and less than 2.70 Å between heavy atoms and hydrogen atoms are listed in Table 8. The shortest contacts [C(1)···O(2)=2.892(26) and H(2)···O(2)=2.32 Å] might be considered indicative of an intermolecular C-H···O hydrogen bond; although the C(1)-H(2)···O(2) angle of 111° is expected to have a large standard deviation, its value is sufficiently far from 180° to make such a bond unlikely.

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Table 8. Intermolecular distances (Å)

O(7)···C(3 ⁱ)	3.146 (16)	O(7)···O(2 ^{iv})	3.091 (27)
O(7)···N(3 ⁱ)	3.135 (21)	C(2)···O(3 ^{iv})	3.204 (28)
O(1)···C(4 ⁱ)	3.152 (15)	N(1)···N(2 ^{iv})	3.162 (31)
O(8)···O(3 ⁱ)	3.269 (18)	H(2)···O(2 ^{iv})	2.32
O(7)···N(7 ⁱ)	3.299 (27)	H(1)···O(2 ^{iv})	2.67
O(7)···H(5 ⁱ)	2.51	C(3)···O(5 ^v)	3.059 (28)
O(1)···H(7 ⁱ)	2.61	C(1)···O(5 ^v)	3.039 (19)
O(8)···C(4 ⁱⁱ)	3.206 (21)	N(2)···O(5 ^v)	3.102 (24)
O(4)···O(2 ⁱⁱⁱ)	3.251 (18)	H(5)···O(5 ^v)	2.48
O(1)···N(4 ⁱⁱⁱ)	3.263 (21)	H(2)···O(5 ^v)	2.54
N(6)···O(3 ⁱⁱⁱ)	3.226 (21)	H(4)···O(6 ^{vi})	2.59
O(1)···O(2 ⁱⁱⁱ)	3.186 (21)	H(2)···O(4 ^{vi})	2.41
O(4)···O(3 ⁱⁱⁱ)	3.062 (21)	H(7)···O(6 ^{vi})	2.43
N(8)···O(2 ^{iv})	3.108 (28)	H(4)···O(4 ^{vi})	2.54
O(1)···O(6 ^{iv})	3.037 (14)		
C(1)···O(2 ^{iv})	2.892 (26)		

The superscripts indicate the equivalent positions as follows:

Superscript			
<i>x</i>	<i>y</i>	<i>z</i>	None
1 + <i>x</i>	1 + <i>y</i>	<i>z</i>	i
1 + <i>x</i>	<i>y</i>	<i>z</i>	ii
<i>x</i>	1 + <i>y</i>	<i>z</i>	iii
<i>y</i>	1 + <i>y</i> - <i>x</i>	- $\frac{1}{2}$ + <i>z</i>	iv
<i>y</i>	<i>y</i> - <i>x</i>	- $\frac{1}{2}$ + <i>z</i>	v
-1 + <i>y</i>	<i>y</i> - <i>x</i>	- $\frac{1}{2}$ + <i>z</i>	vi

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