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# Crystal structure of a 1:1 cocrystal of nicotinamide with 2-chloro-5-nitrobenzoic acid

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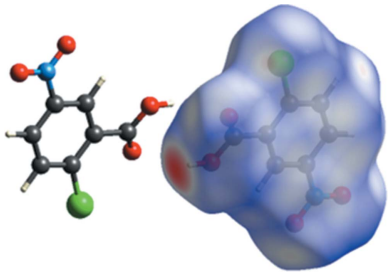
In the title 1:1 cocrystal, $C_7H_4ClNO_4\cdot C_6H_6N_2O$, nicotinamide (NIC) and 2-chloro-5-nitrobenzoic acid (CNBA) cocrystallize with one molecule each of NIC and CNBA in the asymmetric unit. In this structure, CNBA and NIC form hydrogen bonds through O—H···N, N—H···O and C—H···O interactions along with N—H···O dimer hydrogen bonds of NIC. Further additional weak $\pi$–$\pi$ interactions stabilize the molecular assembly of this cocrystal.

## 1. Chemical context

Nicotinamide (NIC) derivatives are used in various applications, for example, in the prevention of type 1 diabetes (Elliott *et al.*, 1993) and nicotinamide cofactors are also used in preparative enzymatic synthesis (Chenault & Whitesides, 1987). The nicotinamide formulation has also been used for treatment in palliative radiotherapy (Horsman *et al.*, 1993). The pharmacological result for the active pharmaceutical ingredient (API) will increase if it becomes cocrystallized with a coformer or other active component (Schultheiss & Newman, 2009; Lemmerer *et al.*, 2010). Chlorobenzoic acid derivatives are widely used in the pharmaceutical industry. 2-Chloro-4-nitrobenzoic acid is used for immunodeficiency diseases as an antiviral and anticancer agent (Lemmerer *et al.*, 2010). In the title compound, NIC is cocrystallized with the CNBA coformer as it acts as an excellent candidate for cocrystallization because of the hydrogen-bond acceptor and donor parts (Dragovic *et al.*, 1995).

## 2. Structural commentary

The title compound CNBA–NIC (1:1) crystallizes in the monoclinic space group $P2_1/c$ with four molecules of NIC and



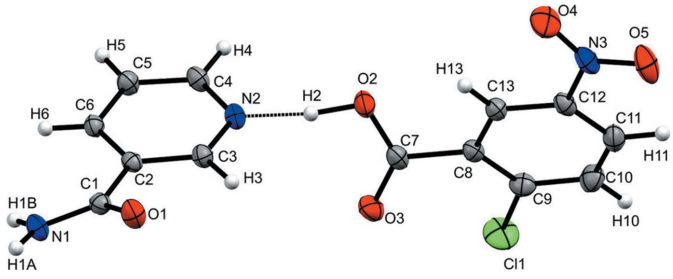



**Figure 1**
The asymmetric unit of the title compound, showing 50% probability ellipsoids, the atom labelling and hydrogen bonding with dotted lines.

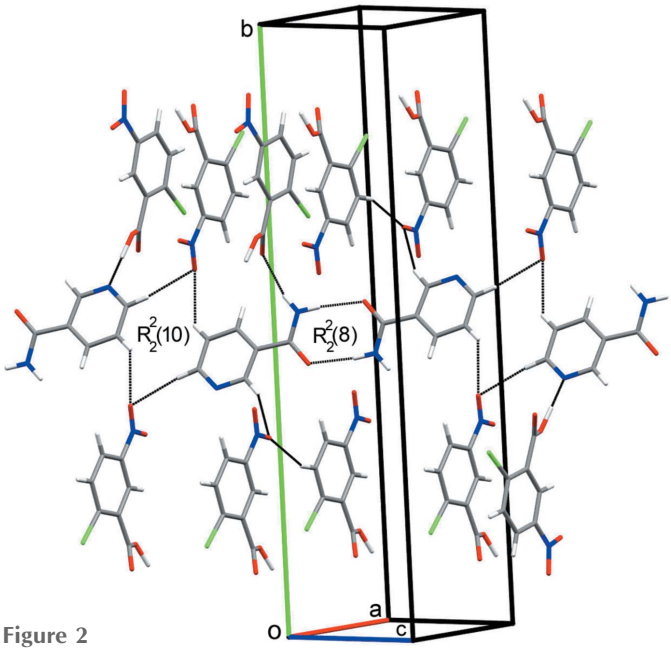



**Figure 2**
Hydrogen bonds in the title compound showing the dimer formation through N—H···O interactions and tetramer formation through C—H···O interactions.

CNBA in the unit cell. The dihedral angle between the amide plane with the mean plane of the phenyl part in NIC is 23.87 (1)°, and the dihedral angles of the carboxyl and nitro groups with the chlorophenyl ring in CNBA are 24.92 (1) and 3.56 (1)°, respectively. In the asymmetric unit, an (CNBA)O–H···N interaction plays a prime role in the molecular recognition of this cocrystal (Fig. 1).

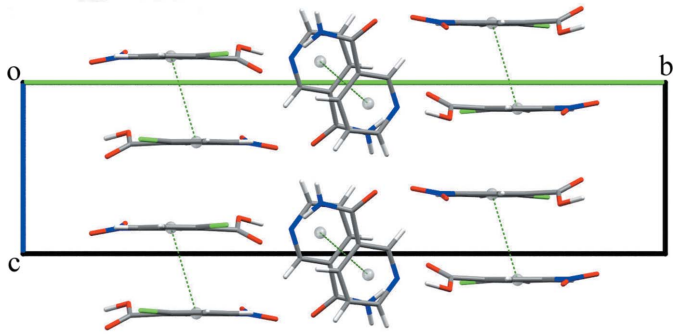



**Figure 3**
Weak $\pi$–$\pi$ interactions stabilize the molecular assembly of both molecules in the crystal.

## 3. Supramolecular features

In the crystal structure of the title cocrystal, a strong (CNBA)O—H···N(NIC) hydrogen bond and additional (NIC)N—H···O(CNBA) and (NIC)C—H···O(CNBA)

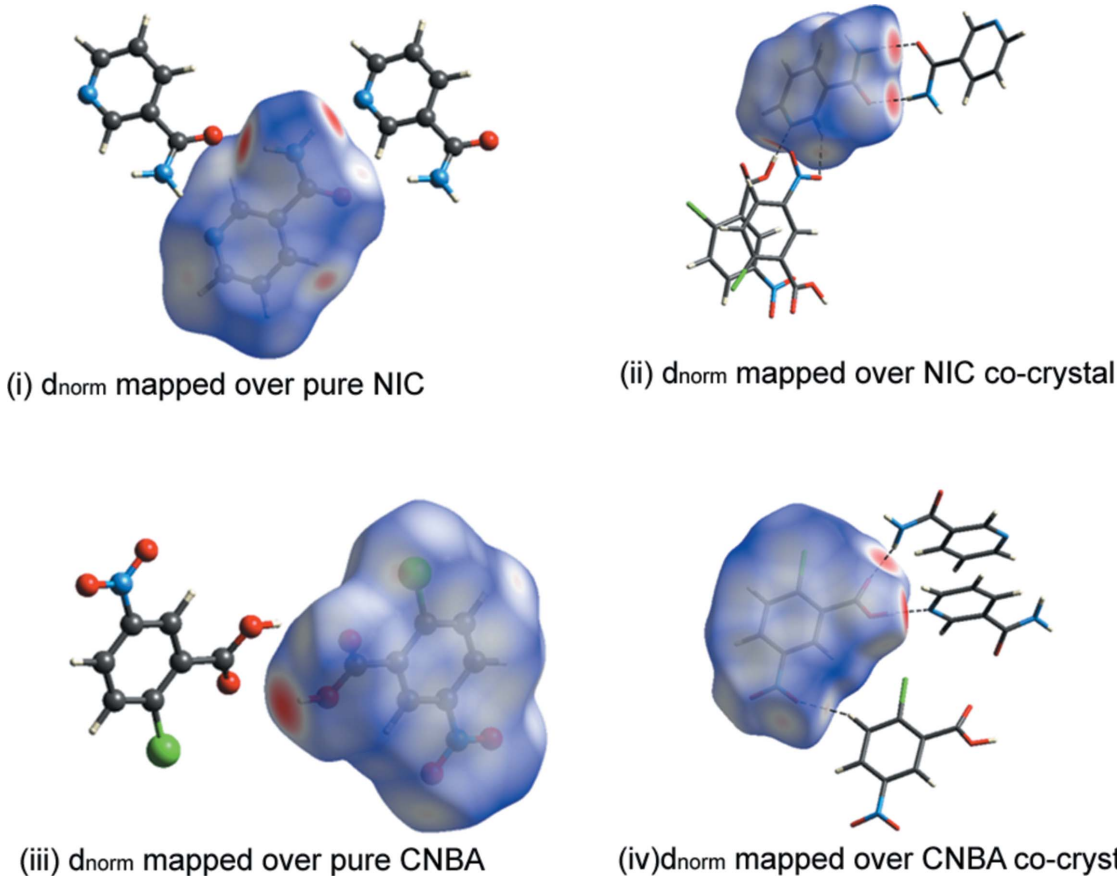
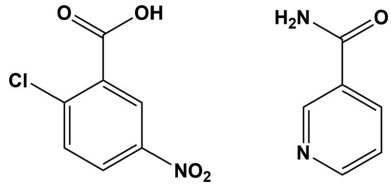



**Figure 4**
Hirshfeld surfaces developed on (i) $d_{norm}$ mapped over the pure NIC molecule, (ii) $d_{norm}$ mapped over the NIC molecule in title compound, (iii) $d_{norm}$ mapped over the pure CNBA molecule and (iv) $d_{norm}$ mapped over the CNBA molecule in title compound.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···O1 | 0.90 (2) | 2.005 (19) | 2.9004 (15) | 171.4 (14) |
| N1—H1*B*···O3 | 0.873 (19) | 2.116 (19) | 2.9715 (14) | 166.6 (16) |
| O2—H2···N2 | 1.07 (2) | 1.49 (2) | 2.5543 (13) | 172 (2) |
| C3—H3···O4 | 0.986 (15) | 2.516 (15) | 3.4505 (16) | 158.2 (12) |
| C4—H4···O5 | 0.979 (14) | 2.442 (15) | 3.3256 (17) | 149.9 (12) |
| C5—H5···O5 | 0.956 (15) | 2.450 (16) | 3.0878 (17) | 124.0 (11) |
| C6—H6···O3 | 0.959 (15) | 2.608 (15) | 3.452 (1) | 147.0 (11) |
| C10—H10···O4 | 0.955 (15) | 2.599 (16) | 3.5010 (18) | 157.6 (15) |

hydrogen bonds are observed (Fig. 2 and Table 1). In this cocrystal, the NIC molecule forms a dimer with itself having an $R_2^2(8)$ graph-set motif (Etter *et al.*, 1990). These dimers are further connected *via* C—H···O hydrogen bonding and form a tetrameric ring with two molecules each of NIC and CNBA with $R_2^2(10)$ graph-set motifs (Etter *et al.*, 1990) (Fig. 2). Furthermore, weak $\pi$–$\pi$ interactions are observed for both NIC [3.68 (7) Å] and CNBA [3.73 (7) Å] which stabilize the molecular assembly along the *bc* plane (Fig. 3).



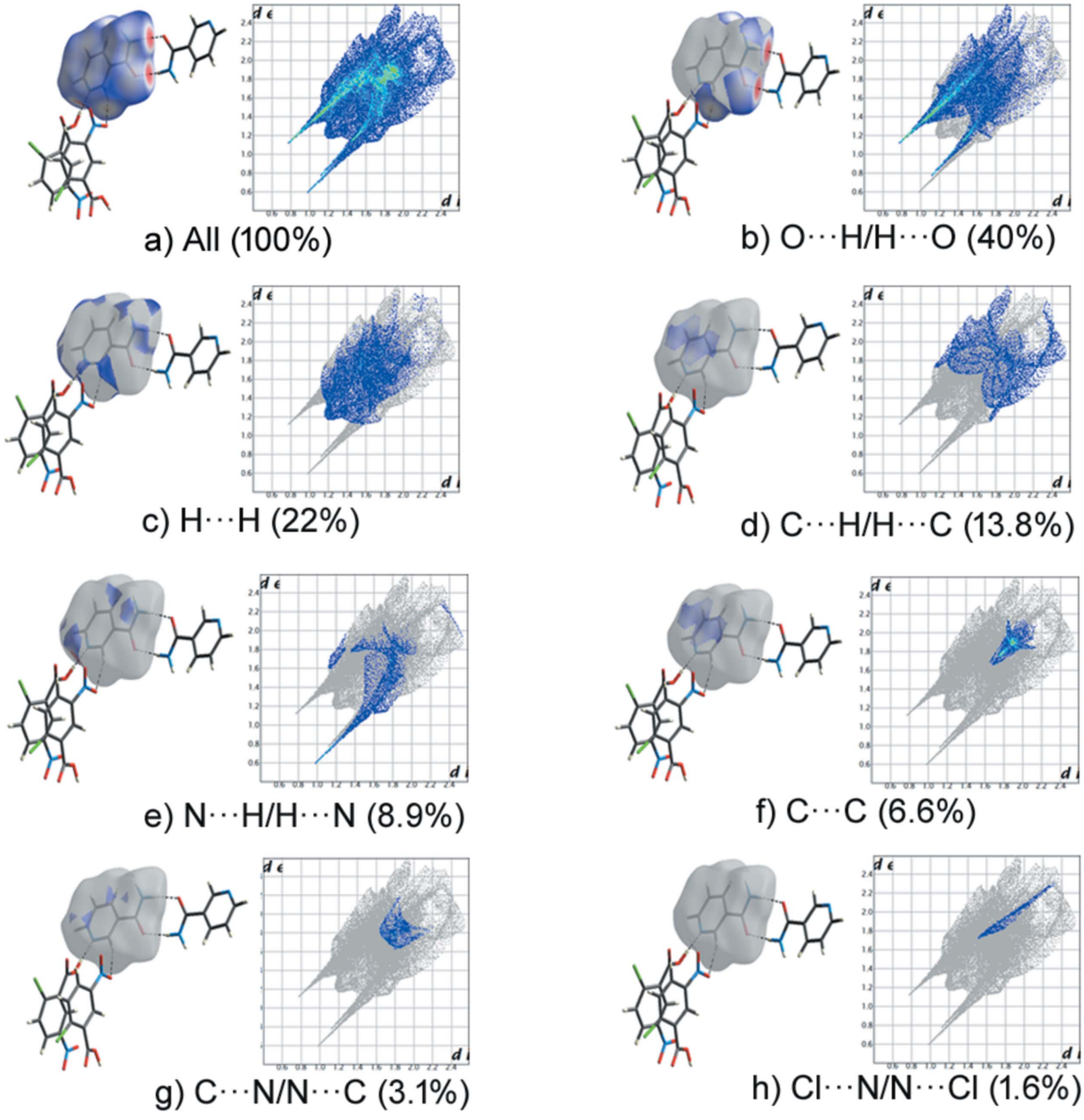




**Figure 5**
Two-dimensional fingerprint plots and relative contributions of various interactions to the Hirshfeld surface of the NIC cocrystal molecule.

## 4. Hirshfeld surface analysis

To understand the role of intermolecular interactions, we have utilized the Hirshfeld surface analysis visualizing tool (Spackman & Jayatilaka, 2009). The Hirshfeld surfaces and two-dimensional fingerprint plots developed using *Crystal-Explorer* (Version 3.1; Wolff *et al.*, 2012) are shown in Fig. 4. The red spot on the surface represents a strong interaction through O—H···N and N—H···O hydrogen bonding, whereas the blue color represents a lack of interaction. The $d_{norm}$ map of the title compound NIC·CNBA and its pure components is shown in Fig. 4, where individual molecular interactions were estimated. The fingerprint plot shows that O···H/H···O and H···H contribute the major part of the interaction in all compounds (Fig. 4). The O···H/H···O contact contributes 40% to the cocrystal NIC molecule (Fig. 5) and 20.5% to the pure NIC molecule (NICOAM01; Miwa *et al.*, 1999) (Fig. 6), and H···H contributes 22% to the cocrystal NIC molecule and 41% to the pure NIC molecule. Similarly, O···H/H···O contacts contribute 33% to the cocrystal CNBA molecule (Fig. 7) and 36.6% to the pure CNBA molecule (CLNBZA; Ferguson & Sim, 1962) (Fig. 8), and H···H contributes 15.2% to the cocrystal CNBA molecule and 17.7% to the pure NIC molecule.

## 5. Database survey

A search for the title cocrystal in the Cambridge Structural Database (CSD, Version 5.40, update of February 2019;

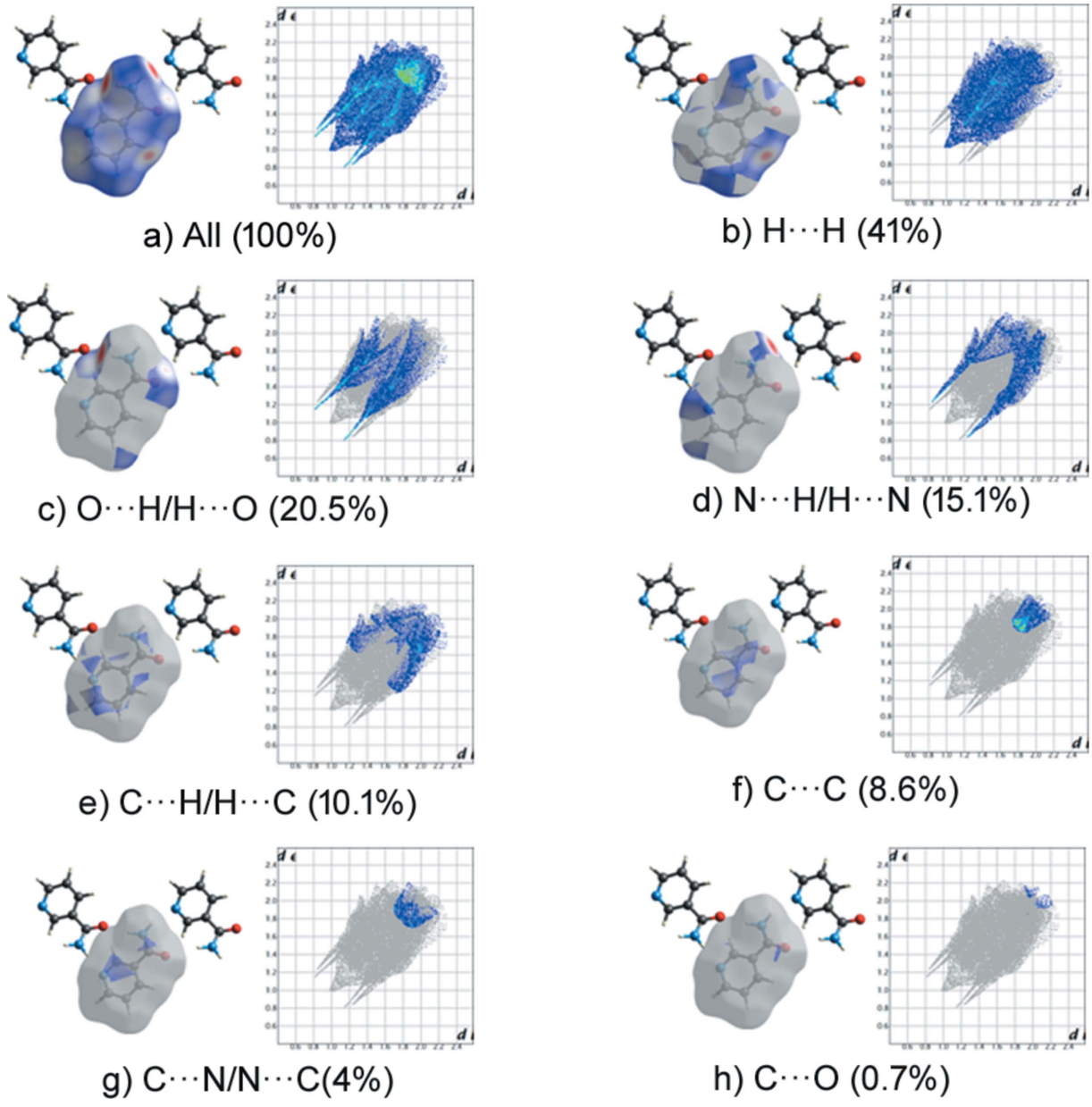



**Figure 6**
Two-dimensional fingerprint plots and relative contributions of various interactions to the Hirshfeld surface of the pure NIC molecule.

Groom *et al.*, 2016) found no hits. However, searches for NIC and CNBA gave 237 and 9 hits, respectively. A search for the NIC molecule showed that the N atom on the phenyl ring forms strong O—H···N hydrogen bonds with a carboxyl H atom in the most of the cocrystals [ABULIU (Lou & Hu, 2011), BICQAH (Aitipamula *et al.*, 2013), BICQEL (Aitipamula *et al.*, 2013), BOBQUG (Zhang *et al.*, 2013), CUYXUQ (Lemmerer & Bernstein, 2010), DINRUP (Lemmerer *et al.*, 2013), DINSEA (Lemmerer *et al.*, 2013), EDAPOQ (Orola & Veidis, 2009) *etc*]. For the CNBA search, two structures were found similar to the title compound where strong hydrogen bonding is formed by the carboxyl H atom with a pyridine N atom [AJIWIA (Gotoh & Ishida, 2009) and OCAZAT (Ishida *et al.*, 2001)]. AJIWIA also shows halogen bonds through C—O···Cl bonding and forms a dimer through C—H···O hydrogen bonding.

## 6. Synthesis and crystallization

All the chemicals used for the synthesis were purchased from Alfa Aesar and used without further purification. A stock solution was prepared from an equimolar mixture of 2-chloro-5 nitrobenzoic acid (82.44 mg, 0.409 mmol) and nicotinamide (50 mg, 0.409 mmol) in a minimum amount of ethanol and made up to a volume of 10 ml. Ten different combinations of the mixture were prepared using ethanol–hexane as the solvent mixture over the ratio range 1:1 to 1:10. The mixture was kept in a 5 ml beaker and covered with parafilm, with four

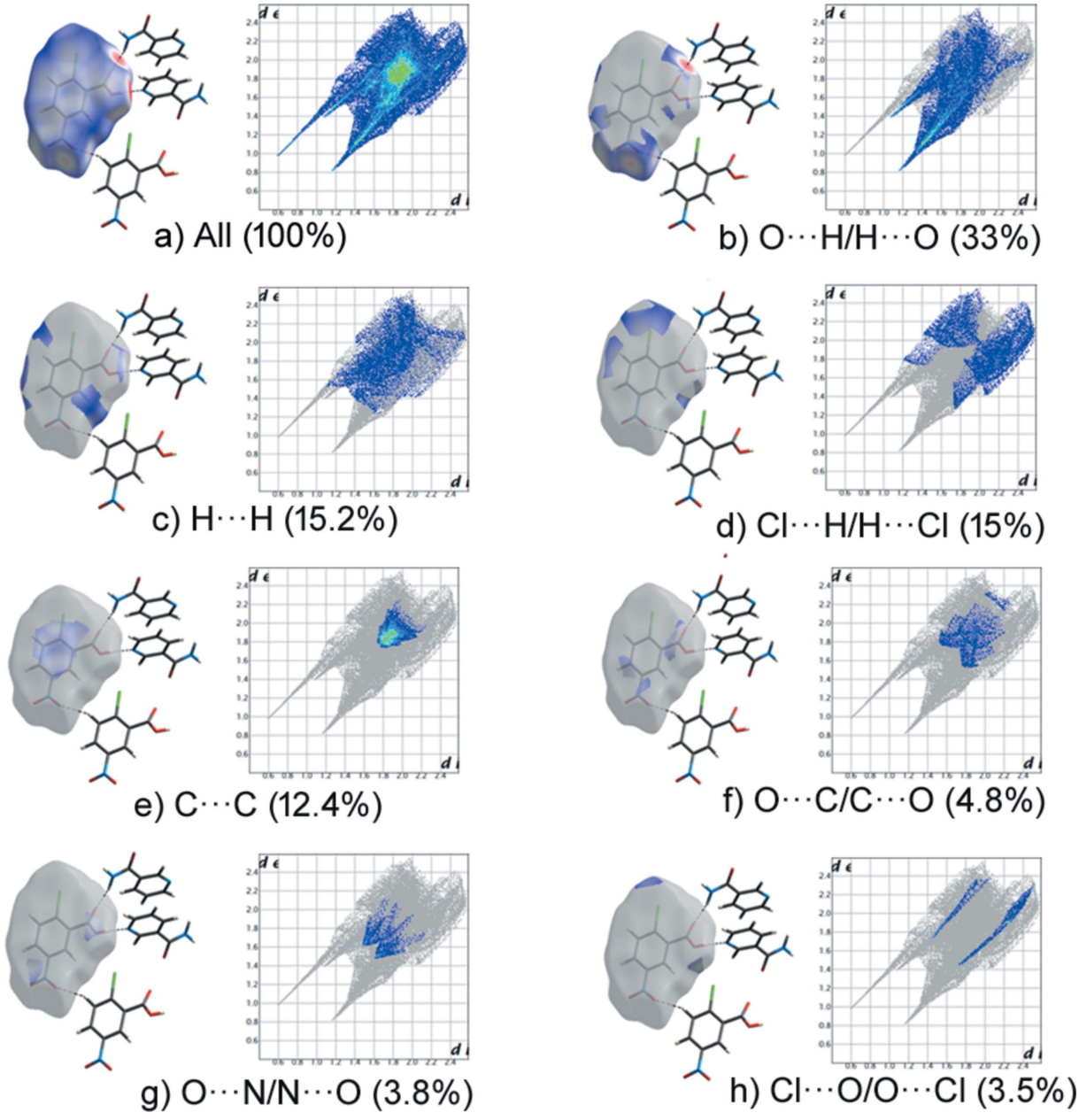



**Figure 7**
Two-dimensional fingerprint plots and relative contributions of various interactions to the Hirshfeld surface of the CNBA cocrystal molecule.

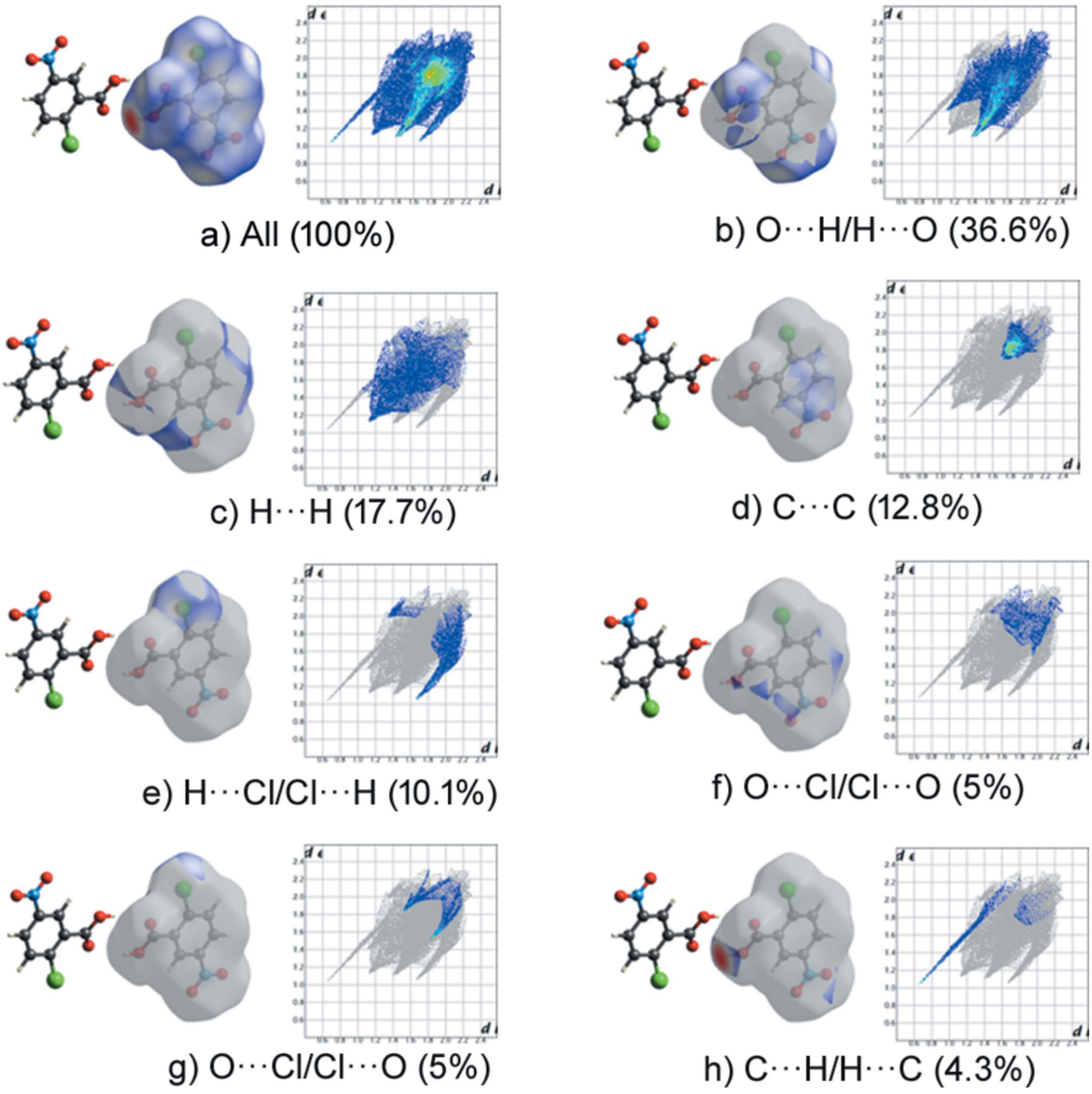



**Figure 8**
Two-dimensional fingerprint plots and relative contributions of various interactions to the Hirshfeld surface of the pure CNBA molecule

to five small holes in it. These solutions were allowed to evaporate slowly at room temperature (27 °C) over several days to obtain single crystals. After a few days, colourless crystals were obtained from ethanol–hexane solutions with concentration ratios of 1:10, 1:2 and 1:4. The melting point of the obtained crystal was 159.7 °C.

## 7. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2. All H atoms were found in a difference Fourier maps and were refind freely.

## Acknowledgements

The authors are thankful to IISER, Bhopal, for the single-crystal X-ray data collection.

## Funding information

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**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_7H_4ClNO_4·C_6H_6N_2O$ |
| $M_r$ | 323.69 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 123 |
| $a, b, c$ (Å) | 7.4897 (1), 26.3607 (5), 7.0623 (1) |
| $\beta$ (°) | 96.356 (1) |
| $V$ (Å$^3$) | 1385.77 (4) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.31 |
| Crystal size (mm) | 0.28 × 0.22 × 0.15 |
| Data collection | |
| Diffractometer | Bruker Kappa APEXII DUO |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2001) |
| $T_{min}$, $T_{max}$ | 0.874, 0.908 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 29950, 4123, 3316 |
| $R_{int}$ | 0.037 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.708 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.038, 0.094, 1.08 |
| No. of reflections | 4123 |
| No. of parameters | 239 |
| H-atom treatment | All H-atom parameters refined |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.30, −0.26 |

Computer programs: *APEX2* (Bruker, 2012), *SAINT* (Bruker, 2012), *SHELXS18* (Sheldrick, 2015), *SHELXL2018* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *OLEX2* (Dolomanov *et al.*, 2009) and *PLATON* (Spek, 2009).


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# supporting information

*Acta Cryst.* (2019). E**75**, 1712-1718 [https://doi.org/10.1107/S2056989019013859]

## Crystal structure of a 1:1 cocrystal of nicotinamide with 2-chloro-5-nitrobenzoic acid

**Keshab M. Bairagi, Priyanka Pal, Subhrajyoti Bhandary, Katharigatta N. Venugopala, Deepak Chopra and Susanta K. Nayak**

### Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXS18* (Sheldrick, 2015); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009) and *PLATON* (Spek, 2009).

### 2-Chloro-5-nitrobenzoic acid–nicotinamide (1/1)

*Crystal data*

$C_7H_4ClNO_4·C_6H_6N_2O$
$M_r$ = 323.69
Monoclinic, $P2_1/c$
$a$ = 7.4897 (1) Å
$b$ = 26.3607 (5) Å
$c$ = 7.0623 (1) Å
$\beta$ = 96.356 (1)°
$V$ = 1385.77 (4) Å$^3$
$Z$ = 4
$F(000)$ = 664
$D_x$ = 1.551 Mg m$^{-3}$
Melting point: 159.7 K
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 4123 reflections
$\theta$ = 1.5–30.2°
$\mu$ = 0.31 mm$^{-1}$
$T$ = 123 K
Block, colorless
0.28 × 0.22 × 0.15 mm

*Data collection*

Bruker Kappa APEXII DUO diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2001)
$T_{min}$ = 0.874, $T_{max}$ = 0.908
29950 measured reflections
4123 independent reflections
3316 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.037
$\theta_{max}$ = 30.2°, $\theta_{min}$ = 1.6°
$h$ = −10→10
$k$ = −37→37
$l$ = −9→9

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.094
$S$ = 1.08
4123 reflections
239 parameters
0 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.4303P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 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**. Single-crystal X-ray diffraction data were collected on a Bruker KAPPA APEX II DUO diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71073Å)(Bruker, 2012). The data collection was performed at 153 (2) K. The temperature was monitored by an Oxford Cryostream cooling system (Oxford Cryostat). the program SAINT (Bruker, 2012) were used for cell refinement and data reduction. The data were scaled and absorption correction performed using SADABS(Bruker, 2001). The structure was solved by direct methods using SHELXS-18(Sheldrick, 2015) and refined by full-matrix least-squares methods based on F2 using SHELXL-2018/3(Sheldrick, 2015). The computing , Mercury(Macrae *et al.*, 2008) and PLATON (Spek, 2009) were used for molecular graphics and molecular interactions. All non-hydrogen atoms were refined anisotropically.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl1 | −0.18141 (5) | 0.18331 (2) | 0.33099 (6) | 0.04137 (12) |
| O2 | 0.39368 (12) | 0.16413 (3) | 0.29015 (14) | 0.0267 (2) |
| O1 | 0.87918 (13) | 0.45197 (3) | 1.35865 (13) | 0.0268 (2) |
| O5 | 0.29333 (16) | 0.39338 (4) | 0.38136 (16) | 0.0381 (3) |
| O3 | 0.16833 (14) | 0.13103 (3) | 0.43221 (14) | 0.0308 (2) |
| O4 | 0.50015 (15) | 0.34087 (4) | 0.32242 (18) | 0.0417 (3) |
| N1 | 0.87836 (15) | 0.53606 (4) | 1.29452 (16) | 0.0226 (2) |
| N2 | 0.57395 (14) | 0.41744 (4) | 0.85619 (15) | 0.0208 (2) |
| N3 | 0.34615 (16) | 0.35059 (4) | 0.35149 (16) | 0.0262 (2) |
| C6 | 0.75383 (15) | 0.50921 (4) | 0.89924 (17) | 0.0189 (2) |
| C1 | 0.83945 (15) | 0.48801 (4) | 1.24921 (17) | 0.0193 (2) |
| C2 | 0.74506 (15) | 0.47734 (4) | 1.05512 (16) | 0.0172 (2) |
| C12 | 0.21719 (17) | 0.30889 (4) | 0.35036 (17) | 0.0209 (2) |
| C4 | 0.59051 (17) | 0.44720 (5) | 0.70484 (18) | 0.0221 (2) |
| C13 | 0.28144 (16) | 0.25993 (4) | 0.35032 (17) | 0.0193 (2) |
| C5 | 0.67736 (17) | 0.49327 (5) | 0.72106 (18) | 0.0217 (2) |
| C9 | −0.02066 (17) | 0.23039 (5) | 0.34499 (19) | 0.0243 (3) |
| C3 | 0.65244 (16) | 0.43172 (4) | 1.02733 (17) | 0.0201 (2) |
| C8 | 0.16239 (16) | 0.21927 (4) | 0.35036 (16) | 0.0191 (2) |
| C10 | −0.08225 (18) | 0.28024 (5) | 0.3432 (2) | 0.0291 (3) |
| C7 | 0.24078 (17) | 0.16659 (4) | 0.36051 (17) | 0.0205 (2) |
| C11 | 0.03681 (19) | 0.32024 (5) | 0.34746 (19) | 0.0261 (3) |
| H3 | 0.639 (2) | 0.4084 (6) | 1.134 (2) | 0.022 (4)* |
| H6 | 0.813 (2) | 0.5415 (6) | 0.909 (2) | 0.022 (4)* |
| H13 | 0.404 (2) | 0.2537 (6) | 0.352 (2) | 0.028 (4)* |
| H4 | 0.540 (2) | 0.4339 (6) | 0.581 (2) | 0.025 (4)* |
| H5 | 0.691 (2) | 0.5138 (6) | 0.612 (2) | 0.026 (4)* |
| H1A | 0.947 (2) | 0.5426 (6) | 1.405 (3) | 0.035 (4)* |
| H1B | 0.850 (2) | 0.5613 (7) | 1.216 (3) | 0.038 (5)* |
| H11 | −0.006 (2) | 0.3550 (7) | 0.346 (3) | 0.040 (5)* |
| H10 | −0.208 (3) | 0.2870 (7) | 0.338 (3) | 0.042 (5)* |
| H2 | 0.462 (3) | 0.1292 (9) | 0.326 (3) | 0.074 (7)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.02685 (18) | 0.0403 (2) | 0.0562 (3) | −0.01523 (14) | 0.00135 (15) | 0.00272 (16) |
| O2 | 0.0251 (5) | 0.0190 (4) | 0.0362 (5) | 0.0037 (3) | 0.0040 (4) | 0.0050 (4) |
| O1 | 0.0362 (5) | 0.0207 (4) | 0.0216 (5) | −0.0011 (4) | −0.0050 (4) | 0.0024 (3) |
| O5 | 0.0529 (7) | 0.0147 (4) | 0.0430 (6) | −0.0008 (4) | −0.0109 (5) | −0.0029 (4) |
| O3 | 0.0424 (6) | 0.0172 (4) | 0.0346 (5) | −0.0037 (4) | 0.0115 (4) | 0.0017 (4) |
| O4 | 0.0345 (6) | 0.0268 (5) | 0.0654 (8) | −0.0094 (4) | 0.0126 (5) | 0.0039 (5) |
| N1 | 0.0265 (5) | 0.0186 (5) | 0.0213 (5) | 0.0006 (4) | −0.0040 (4) | −0.0017 (4) |
| N2 | 0.0211 (5) | 0.0163 (5) | 0.0243 (5) | −0.0016 (4) | −0.0008 (4) | −0.0014 (4) |
| N3 | 0.0357 (6) | 0.0165 (5) | 0.0253 (6) | −0.0031 (4) | −0.0022 (4) | 0.0021 (4) |
| C6 | 0.0196 (5) | 0.0151 (5) | 0.0220 (6) | −0.0004 (4) | 0.0022 (4) | −0.0009 (4) |
| C1 | 0.0187 (5) | 0.0192 (6) | 0.0200 (6) | 0.0007 (4) | 0.0023 (4) | −0.0015 (4) |
| C2 | 0.0167 (5) | 0.0164 (5) | 0.0184 (5) | 0.0018 (4) | 0.0015 (4) | −0.0014 (4) |
| C12 | 0.0275 (6) | 0.0164 (5) | 0.0184 (6) | −0.0018 (4) | 0.0006 (4) | 0.0000 (4) |
| C4 | 0.0247 (6) | 0.0197 (6) | 0.0207 (6) | 0.0010 (5) | −0.0022 (5) | −0.0025 (4) |
| C13 | 0.0209 (5) | 0.0183 (5) | 0.0186 (6) | −0.0003 (4) | 0.0011 (4) | 0.0004 (4) |
| C5 | 0.0268 (6) | 0.0184 (6) | 0.0194 (6) | 0.0004 (4) | 0.0006 (5) | 0.0017 (4) |
| C9 | 0.0216 (6) | 0.0256 (6) | 0.0257 (6) | −0.0044 (5) | 0.0025 (5) | 0.0000 (5) |
| C3 | 0.0216 (5) | 0.0173 (5) | 0.0212 (6) | −0.0002 (4) | 0.0015 (4) | 0.0001 (4) |
| C8 | 0.0216 (5) | 0.0177 (5) | 0.0177 (6) | −0.0017 (4) | 0.0012 (4) | −0.0002 (4) |
| C10 | 0.0217 (6) | 0.0320 (7) | 0.0335 (7) | 0.0045 (5) | 0.0027 (5) | 0.0004 (5) |
| C7 | 0.0266 (6) | 0.0167 (5) | 0.0174 (6) | −0.0019 (4) | −0.0011 (4) | −0.0008 (4) |
| C11 | 0.0305 (7) | 0.0218 (6) | 0.0255 (7) | 0.0061 (5) | 0.0010 (5) | −0.0004 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C9 | 1.7244 (13) | C1—C2 | 1.4977 (16) |
| O2—C7 | 1.2994 (15) | C2—C3 | 1.3913 (16) |
| O2—H2 | 1.07 (2) | C12—C13 | 1.3774 (16) |
| O1—C1 | 1.2399 (14) | C12—C11 | 1.3816 (18) |
| O5—N3 | 1.2215 (15) | C4—C5 | 1.3766 (17) |
| O3—C7 | 1.2208 (14) | C4—H4 | 0.977 (16) |
| O4—N3 | 1.2209 (16) | C13—C8 | 1.3941 (16) |
| N1—C1 | 1.3307 (16) | C13—H13 | 0.932 (16) |
| N1—H1A | 0.901 (19) | C5—H5 | 0.957 (16) |
| N1—H1B | 0.876 (18) | C9—C10 | 1.3921 (19) |
| N2—C3 | 1.3383 (16) | C9—C8 | 1.3984 (17) |
| N2—C4 | 1.3426 (16) | C3—H3 | 0.984 (15) |
| N3—C12 | 1.4626 (16) | C8—C7 | 1.5064 (16) |
| C6—C5 | 1.3887 (17) | C10—C11 | 1.379 (2) |
| C6—C2 | 1.3922 (16) | C10—H10 | 0.955 (18) |
| C6—H6 | 0.959 (15) | C11—H11 | 0.971 (18) |
| | | | |
| C7—O2—H2 | 111.9 (13) | C12—C13—H13 | 120.6 (9) |
| C1—N1—H1A | 118.6 (11) | C8—C13—H13 | 119.6 (9) |
| C1—N1—H1B | 122.7 (12) | C4—C5—C6 | 119.08 (11) |

| | | | |
|---|---|---|---|
| H1A—N1—H1B | 118.4 (16) | C4—C5—H5 | 121.5 (9) |
| C3—N2—C4 | 118.98 (10) | C6—C5—H5 | 119.4 (9) |
| O4—N3—O5 | 123.56 (12) | C10—C9—C8 | 121.40 (11) |
| O4—N3—C12 | 118.49 (11) | C10—C9—Cl1 | 116.76 (10) |
| O5—N3—C12 | 117.95 (12) | C8—C9—Cl1 | 121.80 (10) |
| C5—C6—C2 | 118.89 (11) | N2—C3—C2 | 122.20 (11) |
| C5—C6—H6 | 118.5 (9) | N2—C3—H3 | 116.1 (9) |
| C2—C6—H6 | 122.6 (9) | C2—C3—H3 | 121.7 (9) |
| O1—C1—N1 | 123.25 (11) | C13—C8—C9 | 117.65 (11) |
| O1—C1—C2 | 118.88 (10) | C13—C8—C7 | 117.57 (10) |
| N1—C1—C2 | 117.87 (11) | C9—C8—C7 | 124.77 (11) |
| C3—C2—C6 | 118.46 (11) | C11—C10—C9 | 120.57 (12) |
| C3—C2—C1 | 117.96 (10) | C11—C10—H10 | 119.3 (11) |
| C6—C2—C1 | 123.47 (10) | C9—C10—H10 | 120.1 (11) |
| C13—C12—C11 | 122.95 (11) | O3—C7—O2 | 124.84 (11) |
| C13—C12—N3 | 118.27 (11) | O3—C7—C8 | 122.60 (11) |
| C11—C12—N3 | 118.78 (11) | O2—C7—C8 | 112.54 (10) |
| N2—C4—C5 | 122.26 (11) | C10—C11—C12 | 117.62 (12) |
| N2—C4—H4 | 116.2 (9) | C10—C11—H11 | 120.6 (11) |
| C5—C4—H4 | 121.6 (9) | C12—C11—H11 | 121.8 (11) |
| C12—C13—C8 | 119.79 (11) | | |

| | | | |
|---|---|---|---|
| C5—C6—C2—C3 | −2.96 (17) | C1—C2—C3—N2 | −175.60 (10) |
| C5—C6—C2—C1 | 173.20 (11) | C12—C13—C8—C9 | 1.77 (17) |
| O1—C1—C2—C3 | 21.57 (16) | C12—C13—C8—C7 | −176.93 (11) |
| N1—C1—C2—C3 | −159.19 (11) | C10—C9—C8—C13 | −1.15 (19) |
| O1—C1—C2—C6 | −154.61 (12) | Cl1—C9—C8—C13 | 176.29 (9) |
| N1—C1—C2—C6 | 24.63 (17) | C10—C9—C8—C7 | 177.44 (12) |
| O4—N3—C12—C13 | 11.29 (17) | Cl1—C9—C8—C7 | −5.12 (18) |
| O5—N3—C12—C13 | −168.81 (12) | C8—C9—C10—C11 | −0.3 (2) |
| O4—N3—C12—C11 | −168.07 (12) | Cl1—C9—C10—C11 | −177.83 (11) |
| O5—N3—C12—C11 | 11.83 (17) | C13—C8—C7—O3 | 151.23 (12) |
| C3—N2—C4—C5 | −3.55 (18) | C9—C8—C7—O3 | −27.36 (19) |
| C11—C12—C13—C8 | −1.03 (19) | C13—C8—C7—O2 | −26.97 (15) |
| N3—C12—C13—C8 | 179.64 (11) | C9—C8—C7—O2 | 154.44 (12) |
| N2—C4—C5—C6 | 1.33 (19) | C9—C10—C11—C12 | 1.0 (2) |
| C2—C6—C5—C4 | 1.97 (17) | C13—C12—C11—C10 | −0.4 (2) |
| C4—N2—C3—C2 | 2.47 (17) | N3—C12—C11—C10 | 178.92 (12) |
| C6—C2—C3—N2 | 0.78 (17) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···O1 | 0.90 (2) | 2.005 (19) | 2.9004 (15) | 171.4 (14) |
| N1—H1*B*···O3 | 0.873 (19) | 2.116 (19) | 2.9715 (14) | 166.6 (16) |
| O2—H2···N2 | 1.07 (2) | 1.49 (2) | 2.5543 (13) | 172 (2) |
| C3—H3···O4 | 0.986 (15) | 2.516 (15) | 3.4505 (16) | 158.2 (12) |
| C4—H4···O5 | 0.979 (14) | 2.442 (15) | 3.3256 (17) | 149.9 (12) |

| | | | | |
|---|---|---|---|---|
| C5—H5···O5 | 0.956 (15) | 2.450 (16) | 3.0878 (17) | 124.0 (11) |
| C6—H6···O3 | 0.959 (15) | 2.608 (15) | 3.452 (1) | 147.0 (11) |
| C10—H10···O4 | 0.955 (15) | 2.599 (16) | 3.5010 (18) | 157.6 (15) |