

A structural and theoretical study of intermolecular interactions in nicotinohydrazide dihydrochloride

Rafal Kruszynski

Institute of General and Ecological Chemistry, Technical University of Łódź,
Zeromskiego 116, 90-924 Łódź, Poland

Correspondence e-mail: rafal.kruszynski@p.lodz.pl

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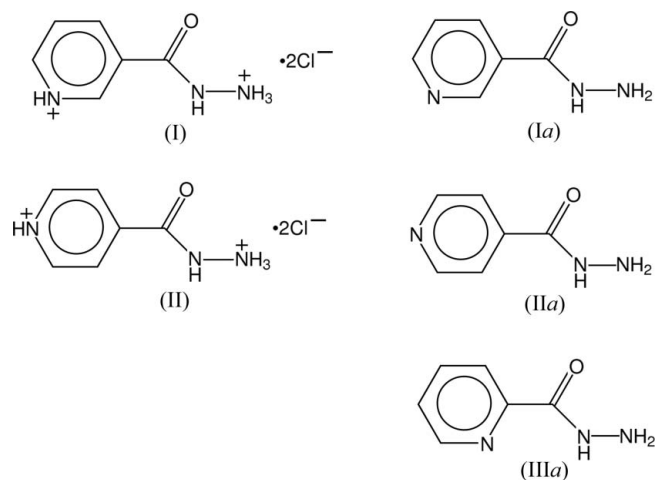
In the title compound [systematic name: 3-(azaniumylcarbamoyl)pyridinium dichloride], $C_6H_9N_3O^{2+} \cdot 2Cl^-$, the ions are connected by $N-H \cdots Cl$ hydrogen bonds to form layers and $C-H \cdots Cl$ interactions expand the layers into a three-dimensional net. The energies of the $N-H \cdots Cl$ interactions range from typical for very weak interactions ($0.17 \text{ kcal mol}^{-1}$) to those observed for relatively strong interactions ($29.1 \text{ kcal mol}^{-1}$). $C-H \cdots Cl$ interactions can be classified as weak and mildly strong (energies ranging from 2.2 to $8.2 \text{ kcal mol}^{-1}$). Despite the short contacts existing between the parallel aromatic rings of the cations, $\pi-\pi$ interactions do not occur.

Comment

Intermolecular interactions play a crucial role in chemical, catalytic and biochemical processes, chemical and crystal engineering, as well as in supramolecular chemistry (Jeffrey & Saenger, 1991; Jeffrey, 1997; Epstein & Shubina, 2002). Over the course of the last century new types of intermolecular interactions, such as $\pi-\pi$, anion $\cdots \pi$, cation $\cdots \pi$ and other interactions, were found and they were extensively studied (Payer *et al.*, 2007; Schnabel *et al.*, 2007), especially their spectral (Tonge *et al.*, 2007; Fecko *et al.*, 2003), structural (Suresh, 2007; Fisher *et al.*, 2007) and thermodynamic (Harmon & Nikolla, 2003; Villar *et al.*, 2003) features. However, the energetic behaviour of intermolecular interactions has not received as much attention as other properties. Energetic characteristics are important because they are responsible for the stability of created assemblies (both supramolecular complexes and in-reaction intermediates) and, consequently, they govern the possibilities of applications of specific intermolecular interactions (Gavezzotti, 2008; Oliveira *et al.*, 2006).

The group of aromatic hydrazides exhibits a wide variety of biological activities, including the effective inhibition of oxidases (Artico *et al.*, 1992) and peroxidases (Ouellet *et al.*,

2004), antifungal and antimicrobial activity (Deep *et al.*, 2010) and anticonvulsant activity (Ragavendran *et al.*, 2007). In addition, these compounds have diverse technical applications, *e.g.* as anticorrosive materials (Al-Hazam, 2010) or stabilizers of polymers (Ahmed Mohamed, 1997). The isomers of nicotinohydrazide are also biologically active: the nicotinohydrazide, (*Ia*), is an effective inhibitor of cyclooxygenase activity of prostaglandin H_2 synthase-2, and the isonicotinohydrazide, (*IIa*), has very potent antitubercular activity (Kruger-Thierner, 1956; Zhang & Young, 1993). The mechanism of the biological activity of (*IIa*) is well known (Bardou *et al.*, 1998), but the route of action of (*Ia*) is still unresolved; thus studies of the intermolecular bonding properties of (*Ia*) can be crucial for both determining the inhibition mechanism and the design of drugs selectively inhibiting enzymatic oxidation reactions. The structures of the *ortho* [(*IIIa*); Wu *et al.*, 2005; Zareef *et al.*, 2006], *meta* [(*Ia*); Priebe *et al.*, 2008; Portalone & Colapietro, 2008] and *para* [(*IIa*); Jensen, 1954; Bhat *et al.*, 1974] isomers of nicotinohydrazide were previously determined, but the supramolecular adducts of (*Ia*) and (*IIIa*) are unknown and a very limited number of supramolecular complexes of such compounds have been reported for (*IIa*) (Meng *et al.*, 2008; BenHamada & Jouini, 2006; Kupfer-Tsoucaris & Tsoucaris, 1964; Gel'mbol'dt *et al.*, 2002; Xie, 2007). Additionally in the literature there are reports of the structures of four metal coordination compounds of (*IIa*) (Hanson *et al.*, 1981; Tsintsadze *et al.*, 1980; Zinner *et al.*, 1979; Jiang *et al.*, 2009) and two of (*Ia*) (Van Hecke *et al.*, 2007; Tsintsadze *et al.*, 1979). Nicotinohydrazide dihydrochloride, (*I*), the protonated form of (*Ia*), has been studied because physiological pH typically is lower than 7 and



thus such protonation occurs in biological systems, and almost all drugs or bioactive molecules undergo protonation before they enter the reaction chain. The chloride was chosen and used as a counter-ion since it is the most typical inorganic anion existing in living organisms, and thus knowledge about the intermolecular interactions between the mentioned species can be crucial in both studies of reaction mechanisms and design-targeted drug molecules based on aromatic hydrazides.

The asymmetric unit of the title compound, (I), contains the inorganic anions acting as counter-ions, balancing the charge of the 3-(azaniumylcarbamoyl)pyridinium cation (Fig. 1). The cation is doubly protonated, similar to isonicotinohydrazide dihydrochloride (Kupfer-Tsoucaris & Tsoucaris, 1964), 4-(hydraziniumcarbonyl)pyridinium hexafluorosilicate (Gel'mbol'dt *et al.*, 2002) and in contrast to monoprotonated dichloro(isonicotinohydrazide)copper(II) hydrochloride (Hanson *et al.*, 1981), (pyridin-4-ylcarbonyl)diazanium 4-(hydrazinocarbonyl)pyridinium bis(dihydrogen phosphate) (Ben-Hamada & Jouini, 2006), *catena*-[bis(μ_2 -isonicotinohydrazido)(isonicotinohydrazido)triaquachlorodimanganese trichloride isonicotinehydrazide solvate] (Tsintsadze *et al.*, 1980) and 4-(hydrazinocarbonyl)pyridinium 3-carboxy-4-hydroxybenzenesulfonate monohydrate (Xie, 2007). The cation of (I) is slightly distorted from planarity (Table 1), with a maximum deviation from the weighted least-squares plane calculated for all its non-H atoms of 0.1421 (11) Å for atom N4. Such a maximum deviation in (Ia) exists for O1 and it is distinctly larger [0.538 Å (Priebe *et al.*, 2008) and 0.541 Å (Portalone & Colapietro, 2008)]. Considerations of (IIa) and its protonated dichloride, (II) (Kupfer-Tsoucaris & Tsoucaris, 1964), show maximum deviations of about 0.4 Å for both compounds, and (IIIa) can be considered planar. Because the intramolecular N—H...N/O hydrogen bonds in (I) and (II) are structurally forbidden [they can only exist in planar (IIIa)], thus it can be supposed that twist of the azaniumylcarbamoyl moiety in (I) is caused mainly by the intermolecular interactions and crystal packing and to a lesser extent by the electronic structure of the cation. The organic cation shows typical values of bond lengths and angles, comparable with the other above cited isomers of nicotinohydrazide, their salts and their complex compounds.

The cations and anions of (I) are held together by N—H...Cl hydrogen bonds (Fig. 2 and Table 2) and they create the *DDDDDC*(2) unitary graph set (Bernstein *et al.*, 1995). At the second-level graph, N_2 , the hydrogen bonds can be expressed as $C_2^1(5)C_2^1(9)C(2)D[R_4^2(10)C_2^1(9)C(2)D]$ basic

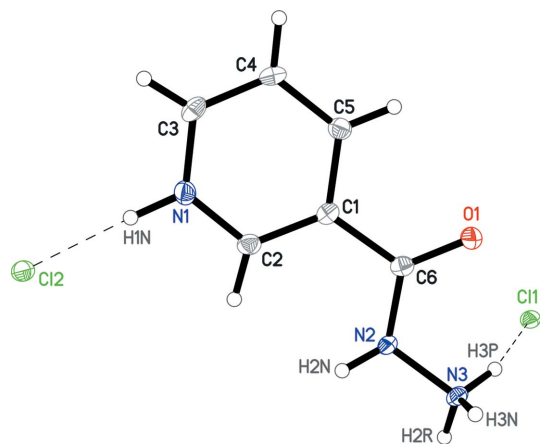


Figure 1

A view of the asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines.

graph sets. In this way, a layer parallel to the crystallographic (100) plane is created. Neighbouring layers are interlinked by short intermolecular C—H...Cl interactions (Table 2), which can be classified as weak hydrogen bonds (Desiraju & Steiner, 1999). In such a manner, a three-dimensional supramolecular structure is created. The hydrogen-bond scheme in (Ia) is distinctly different due to both the absence of a hydrogen-bond ionic acceptor (Cl^-) and the presence of two potential hydrogen-bond acceptors ($-\text{NH}_2$ and N^+) instead of two additional hydrogen-bond donors ($-\text{NH}_3^+$ and NH^+). The first-level graph set of (Ia) is expressed by the *C*(5)*C*(5)*C*(6) descriptor. A hydrogen-bonding scheme similar to that in (I) exists in (II): $N_1 = \text{DDDD}$. The main dissimilarity originates from the different position of the protonated N atom in the aromatic ring and the creation of two-centre hydrogen bonds in (II) in contrast to two- and three-centre hydrogen bonds in (I). There are short contacts between the parallel aromatic rings of cations of (I) [the symmetry-generated rings are obtained by $(-x + 1, -y + 1, -z)$ and $(-x + 1, -y + 1, -z + 1)$ symmetry transformations; the distances between ring centroids are 3.805 (2) and 4.054 (2) Å, respectively], but the possibility of π - π interactions was rejected on geometric grounds (neighbouring aromatic bonds do not overlap sufficiently).

The molecular electronic properties have been calculated at a single point for both the diffraction-derived coordinates and the optimized structure, and the geometric parameters are comparable within three standard deviations, although the geometrically optimized molecules show typical elongation of the N—H and the C—H bonds (from 0.07 to 0.16 Å). The total binding energies of intermolecular interactions were calculated for molecular sets containing from one to eight cation-anion pairs with usage of total self-consistent field energy. The cations and anions within each molecular set were arranged as

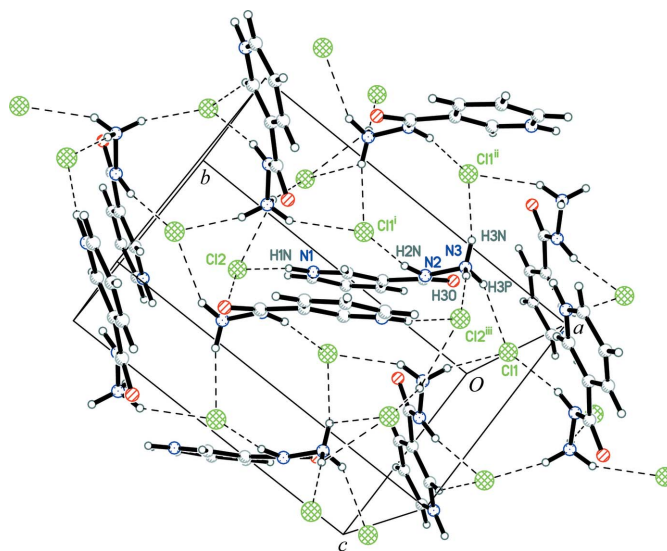


Figure 2

Part of the molecular packing of (I), showing the N—H...Cl hydrogen bonds (lines) creating the layer parallel to the crystallographic (100) plane. The symmetry codes are as given in Table 2.

in hydrogen-bonded layers, along interlayer C—H...Cl intermolecular interactions and along piles created by cations. The structural parameters (with H-atom positions geometrically optimized) were a starting model in each calculation. To calculate the electrostatic interaction energy between anions and cations, additional computations were performed for subsets containing an odd number of cations and anions (such calculated interaction energy is composed of a purely electrostatic term associated with formal +1 and -1 charges and from total intermolecular interaction energy between uncharged molecules, thus the subtraction of the energy value calculated for uncharged subsets from analogous charged subsets gives the purely electrostatic interaction energy between ions, E_{electr} , Table 2). Basis-set superposition error (BSSE) corrections were carried out using the counterpoise (CP) method (Boys & Bernardi, 1970). The B3LYP functional (Becke, 1993; Lee *et al.*, 1988) and Hartree-Fock calculation followed by a Møller-Plesset correlation energy correction (Møller & Plesset, 1934) truncated at second-order (Head-Gordon *et al.*, 1988) in the triple- ζ 6-311++G(3df,2p) basis set was used, as implemented in GAUSSIAN03 (Frisch *et al.*, 2004). In all cases, the differences in electronic properties and energies originating from the different number of cation-anion pairs used in the calculation and the differences between the above-described methods are given in parentheses as standard deviations of the mean values. Where a deviation is not given, the values were the same within their range of reported precision.

As expected, the cations and anions of (I) are attracted by strong electrostatic interactions with binding energies ranging from 65 to 113 kcal mol⁻¹, and the interaction energy strongly depends on the geometric arrangement of ions (Table 2). Noteworthy is the fact that electrostatic attraction between the hydrogen-bonded layers parallel to the crystallographic (100) plane is distinctly weaker than that existing within the layers. The electrostatic repulsion between the organic cations related by the twofold screw axis at ($\frac{1}{2}$, b , $\frac{1}{4}$) (along C3—H3...O1^v interactions; symmetry code as in Table 2) is about -159 kcal mol⁻¹. The values of N—H...Cl hydrogen-bond energies lie in ranges observed for similar systems such as 2,4-dinitrophenylhydrazine hydrochloride hydrate (Kruszynski, 2008), *o*-tolidinium dichloride dihydrate (Kruszynski, 2009a), 5-(2-halogenoethoxy)-2,3-dihydro-1,4-benzodioxines (Kruszynski, 2009b), 2,3-dihydro-1,3-benzothiazol-2-iminium monohydrogen sulfate, 2-iminio-2,3-dihydro-1,3-benzothiazole-6-sulfonate (Kruszynski & Trzesowska-Kruszynska, 2009), 2-amino-5-chloro-1,3-benzoxazol-3-ium inorganic salts (Kruszynski & Trzesowska-Kruszynska, 2010), 2,3-dihydro-1,3-benzothiazol-2-iminium hydrogen oxydiacetate (Trzesowska-Kruszynska & Kruszyński, 2009), but these energies are larger than typical ones observed for N—H...Cl bonds of non-ionic species. Because the energies of the hydrogen bonds containing donor atoms possessing a formal +1 charge (N1 and N3) are not distinctly stronger than those geometrically similar ones having a formal neutral charge (*e.g.* N2—H2N...Clⁱ and N3—H3N...Clⁱⁱ hydrogen bond; symmetry codes as in Table 2), it can be postulated that the energy

increase is caused mainly by the larger negative charge of ionic chlorine [for both anions -0.94 (6) a.u. (a.u. is the atomic unit defined as the absolute value of one electron charge = 1.602176487 (40) × 10⁻¹⁹ C) derived from analysis of the atomic charges based on the Breneman radii (Breneman & Wiberg, 1990)] in comparison to covalently bonded chlorine, and to a distinctly lesser extent by the larger positive charge on the H atoms of the protonated amine group [from 0.50 (4) to 0.56 (3) a.u. calculated as above] in comparison to neutrally charged groups. Thus, the hydrogen-bond acceptor-donor electron-density sharing in (I) is more preferred than in compounds containing non-ionic species (Kruszynski, 2009b) and, for creation of stronger hydrogen bonds, the additional electron density on a hydrogen-bond acceptor is more important than electron-density deficiency on a hydrogen-bond donor. The strength of the hydrogen bonds does not correlate directly with the enlargement of the $D\cdots A$ distance or $D-H\cdots A$ angle, but a general relationship of increasing hydrogen-bond energy with both decreasing $D\cdots A$ distance and increasing $D-H\cdots A$ angle is observed (Fig. 3). The flattening of the surface of the function $E(D\cdots A, D-H\cdots A)$ at lower angles confirms the postulate that the orientation of the $D-H$ bond relative to the line linking donor and acceptor is more important in the creation of stronger hydrogen bonds than the $D\cdots A$ distance (Kruszynski, 2008), *e.g.* at a $D-H\cdots A$ angle of 100°, all hydrogen-bond energies vanish regardless of $D\cdots A$ distances, and at a $D\cdots A$ distance of 3.6 Å, the increase in the $D-H\cdots A$ angle leads to an increase in hydrogen-bond energy.

For both types of donors (N—H and C—O) the hydrogen-bond geometric parameters and energy undergo the same dependence; thus, the relatively short, but with a narrow angle, N3—H3O...Cl^{iv} hydrogen bond (symmetry code as in Table 2) is distinctly weaker than the longer but more linear C—H...Cl hydrogen bond. The C—H...Cl hydrogen-bond

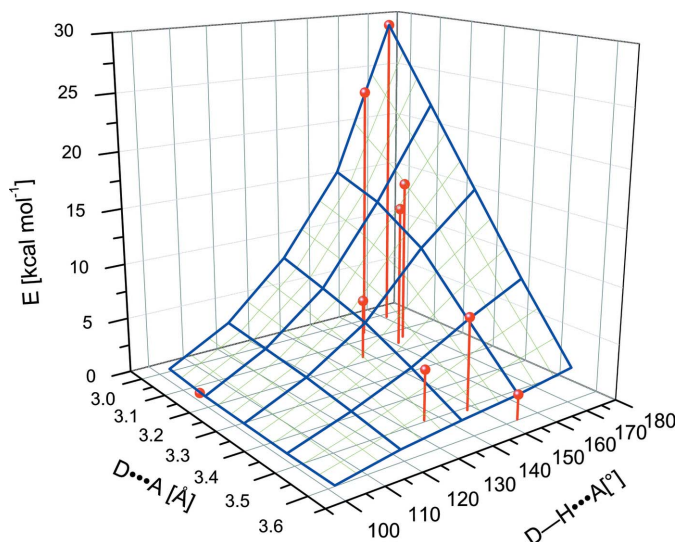


Figure 3
A surface plot showing the relationship between hydrogen-bond energy (E , Table 2) and $D\cdots A$ distances/ $D-H\cdots A$ angles. The values of E are indicated by dots.

energy is relatively large and for the C5—H5···Cl2^{vi} hydrogen bond (symmetry code as in Table 2) it is distinctly greater than the most typical values (about 4 kcal mol⁻¹; Desiraju & Steiner, 1999) as a result of a large negative charge located on the Cl⁻ atom and in consequence the transfer of a considerable amount of electron density to the C—H donor of the hydrogen bond. It must be noted that the geometrically allowed C3—H3···O1^v hydrogen bond (symmetry code as in Table 2) is actually a nonbonding interaction. The nonbonding character of this interaction in comparison to the less linear and longer C—H···Cl bonding interactions again is proof that charge located on hydrogen-bond acceptor atoms has crucial importance for the creation of strong hydrogen bonds. The calculations of the intermolecular interaction energy of parallel aromatic rings related by $(-x + 1, -y + 1, -z + 1)$ and $(-x + 1, -y + 1, -z)$ symmetry transformations show that these interactions are antibonding in character even if the dispersion energy is introduced to the calculations. This confirms the absence of π - π stacking interactions in (I).

The noncovalent nature of the intermolecular interactions in (I) was analysed by the natural bond orbital (NBO) method (Foster & Weinhold, 1980; Reed & Weinhold, 1985; Reed *et al.*, 1988). In this method, the strength of the donor-acceptor charge-transfer delocalization is characterized by the second-order stabilization energy, E_{del} . For hydrogen bonds the principal charge-transfer interactions $E_{\text{del}}(1)$ occur between the chloride lone pairs and the antibonding orbitals of the N—H and C—H bonds. In the lateral charge-transfer interactions, the chloride lone pairs donate their electron density to the one-centre Rydberg orbitals of the H atom. Noteworthy is the fact that interactions between lone-pair orbitals and Rydberg orbitals in C—H···Cl bonds contribute more to total hydrogen-bond energy than in N—H···Cl bonds. Thus, changing the relatively strong N—H hydrogen-bond donor to the weak one (C—H) leads to redistribution of donor electron density and diminishes the energy of constituent interactions containing antibonding orbitals. Because the electron density of the hydrogen-bond acceptor is transferred from donor antibonding orbitals to donor Rydberg orbitals, the total energy of geometrically similar C—H···Cl and N—H···Cl hydrogen bonds is comparable.

Table 2

Experimental hydrogen-bond geometry (Å, °).

Total energy E (kcal mol⁻¹), principal 'delocalization' energy $E_{\text{del}}(1)$ calculated on the NBO basis and electrostatic interaction energy between ions E_{electr} . See *Comment* for a detailed description of the abbreviations and methods used.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$	E	E_{del}	E_{electr}
N1—H1N···Cl2	0.97 (2)	2.05 (2)	3.0149 (14)	171.0 (16)	29.14 (8)	21.4 (3)	82.33 (8)
N2—H2N···Cl1 ⁱ	0.88 (2)	2.28 (2)	3.1359 (14)	165.1 (17)	15.11 (10)	12.0 (4)	95.87 (7)
N3—H3N···Cl1 ⁱⁱ	0.90 (2)	2.29 (2)	3.1596 (15)	161.3 (16)	13.16 (9)	9.7 (3)	103.17 (9)
N3—H3P···Cl1	0.90 (2)	2.38 (2)	3.1772 (15)	147.6 (16)	5.47 (2)	4.51 (12)	102.14 (7)
N3—H3O···Cl2 ⁱⁱⁱ	0.92 (2)	2.19 (2)	3.0641 (14)	158.4 (17)	23.48 (16)	19.8 (8)	84.47 (8)
N3—H3O···Cl2 ^{iv}	0.92 (2)	2.817 (19)	3.1393 (13)	101.9 (13)	0.172 (2)	0.170 (18)	112.96 (7)
C2—H2···Cl1 ⁱ	0.94 (2)	2.73 (2)	3.5971 (16)	153.7 (15)	2.18 (4)	1.78 (9)	95.87 (7)
C3—H3···O1 ^v	0.93 (2)	2.51 (2)	3.4315 (19)	172.7 (16)	†		-159.2 (8)
C4—H4···Cl1 ^v	0.92 (2)	2.77 (2)	3.4948 (16)	136.2 (15)	4.439 (18)	2.89 (2)	65.34 (6)
C5—H5···Cl2 ^{vi}	0.95 (2)	2.671 (19)	3.5098 (16)	147.8 (15)	8.169 (9)	5.14 (2)	65.59 (6)

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

Experimental

Compound (I) (0.001 mol, 0.2101 g) was dissolved in a hot aqueous standard solution of HCl (20 ml, 0.2 mol dm⁻³). The solution was stored in a gaseous HCl atmosphere and after six weeks crystals suitable for measurement had grown in 94% yield.

Crystal data

C ₆ H ₉ N ₃ O ²⁺ ·2Cl ⁻	$V = 869.75 (13) \text{ \AA}^3$
$M_r = 210.06$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.4516 (7) \text{ \AA}$	$\mu = 0.70 \text{ mm}^{-1}$
$b = 12.5202 (12) \text{ \AA}$	$T = 90 \text{ K}$
$c = 7.5020 (6) \text{ \AA}$	$0.21 \times 0.20 \times 0.18 \text{ mm}$
$\beta = 101.559 (4)^\circ$	

Data collection

Kuma KM-4-CCD diffractometer	12309 measured reflections
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 1999)	1657 independent reflections
$T_{\text{min}} = 0.860, T_{\text{max}} = 0.889$	1598 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	136 parameters
$wR(F^2) = 0.065$	Only H-atom coordinates refined
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
1657 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C6—O1	1.2174 (19)	N2—N3	1.4269 (18)
C6—N2	1.362 (2)		
Cl1—C6—N2—N3	-170.21 (12)		

The H atoms were found from difference Fourier syntheses after eight cycles of anisotropic refinement. All H-atom positions were refined freely and the U values were set at $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ in all (including the final) refinement cycles. The isotropic displacement parameters of the H atoms were then refined to check the correctness of their positions. After eight cycles, the refinement reached stable convergence with isotropic displacement parameters in the range 0.0147–0.0313. The values of the isotropic displacement parameters of the H atoms have reasonable values, proving the correctness of the H-atom positions.

Data collection: *CrysAlis CCD* (UNIL IC & Kuma, 2000); cell refinement: *CrysAlis RED* (UNIL IC & Kuma, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 2008) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: UK3027). Services for accessing these data are described at the back of the journal.

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