Structural characterization of hydrogen bonding for antipyrine derivatives: Single-crystal X-ray diffraction and theoretical studies

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Abstract

Objectives. The paper is devoted to the crystal structure characterization of 5-methyl-2-phenyl-4H-pyrazol-3-one (compound I) and 2-(4-chlorophenyl)-5-methyl-4H-pyrazol-3-one (compound II). Methods. Single-crystal X-ray diffraction studies and theoretical calculations: Density functional theory and quantum theory of atoms in molecules. Results. In the solid state, the crystal structure of compound I is characterized by the alternation of OH and NH tautomers connected via O–H---O and N–H---N hydrogen bonds. For compound II, the existence of chains built from the NH monomers via hydrogen bonding can be explained by the peculiarities of cooperative effects. In the framework of quantum theory of atoms in molecules, the following topological characteristics are calculated for all dimers: electron density, Laplacian of electron density, density of kinetic, potential, and total energy in the critical point of the intermolecular hydrogen bond. It is concluded that the hydrogen bond in dimers 1–4, 7 (compound I), and 8–11 (compound II) can be assigned to the intermediate (between covalent and dispersion types) interaction owing to hydrogen bond formation with the participation of electronegative oxygen- (and/or nitrogen-) atoms, whereas H-bond in dimers 5 and 6 (compound I) can be attributed to the dispersion one (no hydrogen bond formation or weak H-bond formation), and it represents the weak interaction, being in agreement with length for intermolecular hydrogen bond in dimers. The electron density and total energy density values demonstrate that the strongest intermolecular H-bonds take place in dimers 1 (OH---O), 4 (OH---O), 7 (OH---N), 8 (OH---O), 9 (NH---N), and 11 (OH---N). The results obtained for compounds I and II are compared with data for antipyrine (1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one; compound III).
**Conclusions.** An important role of intermolecular hydrogen bonding in the crystal packing, molecule association and self-organization via dimer- or more extended species formation has been demonstrated.

**Keywords:** antipyrine and its derivatives, 5-methyl-2-phenyl-4H-pyrazol-3-one, 2-(4-chlorophenyl)-5-methyl-4H-pyrazol-3-one, tautomers, hydrogen bonding, density functional theory (DFT) and quantum theory of atoms in molecules (QTAIM) calculations, crystal structure

For citation: Rukk N.S., Shamsiev R.S., Albov D.V., Mudretsova S.N. Structural characterization of hydrogen bonding for antipyrine derivatives: Single-crystal X-ray diffraction and theoretical studies. Tonk. Khim. Tekhnol. = Fine Chem. Technol. 2021;16(2):113–124. https://doi.org/10.32362/2410-6593-2021-16-2-113-124

**НАУЧНАЯ СТАТЬЯ**

**Структурное описание водородной связи в производных антипирина: рентгеноструктурные и теоретические исследования**

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**Аннотация**

**Цели.** Работа посвящена рассмотрению особенностей кристаллического строения для 5-метил-2-фенил-4Н-пиразол-3-она, I, и 2-(4-хлорфенил)-5-метил-4Н-пиразол-3-она, II, в сравнении с результатами теоретических расчетов.

**Методы.** Рентгеноструктурный анализ и расчеты в рамках теории функционала плотности и квантовой теории атомов в молекулах.

**Результаты.** Показано, что кристаллическая структура I в твердом агрегатном состоянии характеризуется альтернацией OH и NH таутомеров, связанных посредством водородных связей O–H---O и N–H---N. Для соединения II существование цепочек из связанных водородной связью мономеров NH объясняется особенностями кооперативных эффектов и с теоретической точки зрения. В рамках квантовой теории атомов в молекулах (QTAIM) для всех димеров в критической точке межмолекулярной водородной связи были рассчитаны топологические параметры: электронная плотность, лапласиан электронной плотности, плотность кинетической, потенциальной и полной энергии. Показано, что водородная связь в димерах 1–4, 7 (соединение I) и 8–11 (соединение II) относится к взаимодействию промежуточного типа (между ковалентным и дисперсионным взаимодействием) за счет образования водородных связей с участием электроотрицательных атомов кислорода (и/или атомов азота), а водородная связь в димерах 5 и 6 (соединение I) – к дисперсионному типу (отсутствие водородной связи или образование слабой N-связи) и представляет собой слабое взаимодействие, что коррелирует с длиной межмолекулярной водородной связи в димерах.

**Выводы.** Показана важная роль межмолекулярной водородной связи в кристаллической упаковке, ассоциации и самоорганизации молекул.
INTRODUCTION

Antipyrine (1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one; compound III) and related compounds are known to possess a number of bioactive properties, such as analgesic and antipyretic ones. They form a large number of complexes with alkaline-, transition-, and rare-earth metals [1–8]. From this point of view, searching for new ligands (including representatives of antipyrine-based ones) is very important [4, 9]. Using the method of computer prognosis based on the Prediction of Activity Spectra for Substances (PASS) system [10], it has been demonstrated that some pyrazolone derivatives, such as 5-methyl-2-phenyl-4H-pyrazol-3-one (compound I) and 2-(4-chlorophenyl)-5-methyl-4H-pyrazol-3-one (compound II), possess a relatively high probability of antimetastatic activity. It should be underlined that the compound properties are determined mainly by the specific features of chemical bonding, including hydrogen bonding and intermolecular interactions, between structural units. These distinguishing features are responsible for the self-organization of ions and molecules in crystal packing with the formation of channels opened to the intercalation of small species, for example, complexes with nericridonic acid (6-amino-1-hydroxyhexylidene-1,1-bisphosphonic acid) showing promise for treating osteogenesis and the Paget’s disease [11]. In the case of solvation (e.g., styryl dyes of the benzoselenazole series), the system of hydrogen bonding makes the structure more rigid compared with the non-solvation one owing to the solvate molecules participation in the hydrogen bond formation [12]. This results in different photocycloaddition reactivity of the solvated and non-solvated compounds and thus a decreased reaction rate for the solvated species. The same has been demonstrated [13] for water molecules and imidazolium salts with respect to the interaction and formation of guest(H$_2$O)@host (ionic liquid [IL]) complexes through strong H-bonds involving the hydrogen atoms of water molecules and nitrogen atoms of IL anions to produce a guest@host supramolecular structure. Many biologically active molecules contain multiple hydrogen-bonding sites; e.g., barbiturates, a class of compounds widely used for their physiological action as sedatives and anticonvulsants, contain both donor and acceptor atoms for multiple hydrogen-bonding formation. It should be underlined that crystal engineering and design allow obtaining different solid state structures in cocrystals of barbiturate and melamine molecules (linear tape, crinkled tape, or cyclic hexamer) [14]. The hydrogen-bonding importance and its impact on drug efficacy have been demonstrated [15]. In this connection the aim of this paper is to explain structural particularities and their comparison with results of theoretical studies for compounds I, II, and III.

EXPERIMENTAL

Compounds I, II (Sigma-Aldrich, St. Louis, Missouri, USA), and III (All-Russian Product Classifier 931335, chem. pure) were first recrystallized from ethanol. Single crystals were grown from saturated aqueous solutions by isothermal evaporation of the solvent at ambient temperature (ca. 20 °C). Thermogravimetric and differential scanning calorimetric (STA-409 Differential Scanning Calorimeter, Netzsch, Germany) measurements were carried out over the temperature range 293–573 K with a heating rate of 10 K/min under a helium atmosphere. Aluminum oxide was used as a reference material.

Computational methods

The tautomers of compounds I and II (Scheme 1) were examined by density functional theory using the Priroda package [16]. Calculations were made using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [17] and TZ2P Gaussian-type basis sets. The solvation effects were estimated in Gaussian 09 [18] using the polarizable continuum model and solvation model based on density (PCM–SMD; water used as solvent, ε = 78.3553). Vibrational harmonic frequency analysis was conducted for the optimized geometries to ensure that a true local minimum was present with no imaginary frequencies. The starting atomic coordinates of compounds were taken from the X-ray refinement results. Convergence criteria for self-consistent field
cycles and geometry optimization were \(1 \times 10^{-6}\) and \(1 \times 10^{-5}\) a.u., respectively. The quantum-topological characteristics of electron density in the critical points of the intermolecular hydrogen bond were calculated in the framework of the quantum theory of atoms in molecules (QTAIM) using the Multiwfn 3.6 program [19].

**Single-crystal X-ray crystallography**

Crystallographic data were collected and refined on CAD-4 EXPRESS diffractometer\(^1\). Data reduction was carried out using XCAD4\(^2\). The following programs were used for theoretical modeling: SHELXS97 for structure solving [20], SHELXL97 for structure refining [20], and Mercury for molecular graphics [21]. The results are given in Table A1 (see Appendix A, pages 125–126).

CCDC 1891632-1891634 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk.

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**RESULTS AND DISCUSSION**

There are three possible tautomers for compounds I and II (CH: I\(_a\), II\(_a\); NH: I\(_b\), II\(_b\); OH: I\(_c\), II\(_c\); Scheme 1, Table 1) [22]. Here we compare theoretical and single-crystal X-ray diffraction data to examine the crystal packing particularities of compounds I–III. The following order of stability for compound-I tautomers in the gas phase was derived from Table 1: I\(_a\) (CH) > I\(_b\) (NH) > I\(_c\) (OH) [22]. The same order of relative stability was theoretically obtained, the results of which are shown in Table 2. Calculation results of Gibbs free energy (\(\Delta G_{298}\)) values considering solvation effects demonstrate a slightly lower energy gap between I\(_a\) and I\(_b\) and a slightly higher energy gap between I\(_b\) and I\(_c\) (0.0, 24.4, and 31.2 vs. 0.0, 9.1, and 28.4 kJ·mol\(^{-1}\), respectively, Table 2). The same tendency can be observed for compound II (Table 2).

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\(^1\) Enraf_Nonius CAD_4 Software. Version 5.0. Delft (The Netherlands): Enraf_Nonius, 1989.

\(^2\) Harms K., Wokadlo S. XCAD4. University of Hamburg, Germany.

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**Scheme 1.** Different possible tautomers for compounds I and II: R = H for the former and R = Cl for the latter.

**Table 1.** Calculated torsion angles (\(\omega, ^\circ\)), heat of formation (\(\Delta H_f\)), relative energies (\(\Delta E\)), and dipole moments (\(\mu\)) of the tautomers for compound I [22]

| Method      | Tautomer | \(\omega, ^\circ\) | \(\omega, ^\circ\) | \(\Delta H_f\) (kJ·mol\(^{-1}\)) or \(\Delta E\) (kJ·mol\(^{-1}\)) | \(\mu\), Debye |
|-------------|----------|-------------------|-------------------|-------------------------------------------------|----------------|
| AM1         | I\(_a\) (CH) | 155.6             | –                 | 0.0                                              | 2.68           |
|             | I\(_b\) (NH) | –130.9            | 88.9              | 51.51                                            | 3.99           |
|             | I\(_c\) (OH) | –142.6            | –                 | 52.80                                            | 2.06           |
| PM3         | I\(_a\) (CH) | 124.3             | –                 | 0.0                                              | 2.46           |
|             | I\(_b\) (NH) | –98.3             | 86.7              | 18.58                                            | 3.73           |
|             | I\(_c\) (OH) | –130.7            | –                 | 34.14                                            | 2.53           |
| HF/6-31G*   | I\(_a\) (CH) | 166.9             | –                 | 0.0                                              | 3.64           |
|             | I\(_b\) (NH) | –134.9            | 73.0              | 36.02                                            | 5.25           |
|             | I\(_c\) (OH) | –132.0            | –                 | 52.01                                            | 2.31           |
| B3LYP/6-31G*| I\(_a\) (CH) | 177.7             | –                 | 0.0                                              | 3.31           |
|             | I\(_b\) (NH) | –149.5            | 63.0              | 32.76                                            | 5.03           |
|             | I\(_c\) (OH) | –140.6            | –                 | 43.97                                            | 2.09           |
Table 2. Calculated torsion angles (ω, °), relative energies (ΔE), Gibbs free energy (ΔG_{298}), Gibbs free energy with PCM–SMD corrections (ΔG_{298,solv}), and dipole moments (µ) for the tautomers of compounds I, II, and III

|          | ω_C(O)–N̈_1–C_8–C_9 | ω_H–N̈_2–N̈_1–C_8 | ΔE | ΔG_{298} | ΔG_{298,solv} | µ   |
|----------|---------------------|-------------------|-----|----------|----------------|-----|
| Ia       | 179.7               | –                 | 0.0 | 0.0      | 0.0             | 3.39|
| Ib       | –149.5              | 61.8              | 19.3| 24.4     | 9.1             | 5.15|
| Ic       | –154.6              | –                 | 26.2| 31.2     | 28.4            | 2.68|
| IIa      | 179.8               | –                 | 0.0 | 0.0      | 0.0             | 5.11|
| IIb      | –148.5              | 63.7              | 20.2| 25.2     | 8.5             | 6.02|
| IIc      | –156.5              | –                 | 26.5| 31.4     | 28.4            | 4.19|
| III      | –127.7              | –                 | –   | –        | –               | 5.36|

We calculated the parameters of dimer formation from the monomers of compounds I and II, and compared the experimental and theoretical results (Table 3). The crystal structure of compound I is characterized by the alternation of Ib and Ic tautomers (Fig. 1a and b) connected via the O–H---O=C and N–H---N hydrogen bonds (r_{O–H---O} = 2.479 Å, r_{N–H---N} = 2.800 Å, Table 3, entries 1 and 2). Extended infinite chains can be observed (Fig. 1b), as confirmed by the calculation results (Table 3, entries 1–7). For the stronger O–H---O H-bonding between the Ib and Ic tautomers (r_{O–H---O} = 2.62 Å, r_{N–H---N} = 2.98 Å, Table 3, entries 1 and 2) the Ib and Ic self-organization in the solid state possibly begins with the formation of the stronger O–H---O H-bonding, followed by the formation of N–H---N one. This can explain the absence of the Ib–Ib (N–H---O), Ia–Ic (O–H---O), Ic–Ic (N–H---N), and Ia–Ia, Ia–Ib (N–H---N) dimers in the solid state (Table 3, entries 3, 4, 7 and 5, 6), as confirmed by the ΔG_{298} values for the tautomer dimerization (Table 3, entries 1–7, column 6).

Fig. 1. Asymmetric unit of compound I with the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, (a); H-bonding between OH- and NH-tautomers (b).
Compound II exists as the NH tautomer (Fig. 2), the molecules of which are linked by N–H---O-type H-bonds \( (r_{N-H-O} = 2.729 \text{ Å}; \text{ Fig. 2a and Table 3, entry 10}) \). This results in the formation of non-interacting extended chains with mutual anti-orientation (Fig. 2b). In the crystalline state, compound II consists of Ib tautomers, not Ia tautomers. The calculated \( \Delta G_{298} \) values for Ib and Ic dimerization (Ia unable to form dimers with strong hydrogen bonding) demonstrate that the Ib–Ic (O-H---O) dimer is the most stable \( (\Delta G_{298} = -13.3 \text{ kJ mol}^{-1}; \text{ Table 3, entries 8 and 10}) \). It is easy to imagine that the elongation of the chain built from the Ib monomers due to H-bonding (Fig. 2) results in energy gain growth with the number of monomers due to the predominance of the enthalpy contribution \( (\Delta H_{298} = -39.2 \text{ kJ mol}^{-1}; \text{ Table 3, entry 10}) \). The formation of chains built from the Ib tautomers is possible, but, in this case, the enthalpy contribution is approximately equal to the entropy contribution (Table 3, entry 3), which can explain the differing mode of monomer alteration for compound I (Ib–Ic [O---H-O] dimer existence).

For all dimers 1–11, the following topology characteristics were calculated using QTAIM theory: electron density \( (\rho) \), Laplacian of electron density \( (\nabla^2 \rho) \), density of kinetic \( (G) \), potential \( (V) \), and total energy \( (H) \) in the critical point of the intermolecular hydrogen bond (Table 4). On the basis of the \( \nabla^2 \rho \) and \( H \) signs as well as the \( V/G (1 < |V/G| < 2) \) ratio, it can be concluded that hydrogen bond in dimers 1–4 and 7–11 can be assigned to the intermediate (between covalent and dispersion types) interaction, whereas the H-bond in dimers 5 and 6 can be assigned to the dispersion interaction, i.e., the weak interaction. Analysis of \( \rho \) and \( H \) values demonstrates that the strongest intermolecular H-bonds take place in dimers 1 (O-H---O), 4 (O-H---O), 7 (O-H---N), 8 (O-H---O), 9 (N-H---N), and 11 (O-H---N). The same dimers are characterized by the shortest X-H---Y distances and by a non-significant increase in the electron localization function \( (\eta) \). By comparing these results with the Gibbs free energy values for dimerization, it can be concluded that the dimer interaction energy is not sufficiently strong to overcome entropy loss during their formation. However, in spite of the H-bond-favorable topology characteristics, the formation of dimers 9 and 11 is unlikely due to the positive \( \Delta G_{298} \) value.

Experimental data for compounds I–III are given in Appendix A (Tables A1–A10, pages 125–137).

Packing for compound III is characterized by the absence of H-bonding and is based on the presumably steric requirements (Fig. 3, Tables A1, A8–A10), the crystallographic parameters of which are consistent with the existing literature [23–25]. The experimental and theoretical results are confirmed by the thermal analysis data. The melting points for the compounds in question are as follows: 397.6–398.4 (I), 431.8–436.3 (II), and 381.5–381.9 K (III), the melting enthalpy being equal to 18.5, 12.3, and ca. 16.7 kJ mol\(^{-1}\) for (I), (II), and (III), respectively. The order of the latter values is possibly due
| Entry | The species label and sketch | H-bond type and length, Å | $\Delta H_{298}$ (calc./exp.) | $-T\Delta S_{298}$ | $\Delta G_{298}$ (kJ mol$^{-1}$) |
|-------|-------------------------------|---------------------------|-----------------------------|------------------|------------------------------|
| 1     | **Ib–Ic dimer (O–HO)**        | **O–H–O**                 | 2.62/2.479                 | −48.4           | 37.6                         | −10.8                        |
| 2     | **Ib–Ic dimer (NH–N)**        | **N–H–N**                 | 2.98/2.800                 | −28.8           | 39.6                         | 10.9                         |
| 3     | **Ib–Ib dimer (NH–O)**        | **N–H–O**                 | 2.81                       | −38.1           | 37.6                         | −0.6                         |
| 4     | **Ia–Ie dimer (O–HO)**        | **O–H–O**                 | 2.65                       | −41.0           | 39.9                         | −1.1                         |

Table 3. Description of dimer formation ($\Delta H_{298}$ is enthalpy and $\Delta S_{298}$ is entropy) from the corresponding monomers of compounds I and II.
| Entry | The species label and sketch | H-bond type and length, Å | $\Delta H_{298}^{calc./exp.}$ | $-T\Delta S_{298}^{calc./exp.}$ | $\Delta G_{298}^{calc./exp.}$ |
|-------|-----------------------------|---------------------------|-----------------------------|-------------------------------|-----------------------------|
| 1     |                             |                           |                             |                               |                             |
| 2     |                             |                           |                             |                               |                             |
| 3     |                             |                           |                             |                               |                             |
| 4     |                             |                           |                             |                               |                             |
| 5     |                             | 3.08                      | −18.8                       | 36.8                          | 18.0                        |
| 6     |                             | N---H-N                   | −20.2                       | 41.8                          | 21.6                        |
| 7     |                             | N---H-O                   | −33.5                       | 33.5                          | 0.1                         |
| 8     |                             | O---H-O                   | −48.7                       | 35.5                          | −13.3                       |
| 9     |                             | N-H---N                   | −28.4                       | 38.6                          | 10.2                        |

Table 3. Continued
Table 3. Continued

| Entry | The species label and sketch | H-bond type and length, Å | $\Delta H_{298}$ (calc./exp.) | $-T\Delta S_{298}$ | $\Delta G_{298}$ |
|-------|------------------------------|---------------------------|-----------------------------|----------------|-----------------|
| 10    | ![IIb–IIb dimer (NH---O)](image) | N-H---O 2.81/2.729 | −39.2 | 35.5 | −3.7 |
| 11    | ![IIe–IIc dimer (N---HO)](image) | N---H-O 2.70 | −36.0 | 44.5 | 8.5 |

Table 4. Topology characteristics and length for the dimer intermolecular hydrogen bond

| Dimer | $\rho$, e·Å$^{-3}$ | $V\rho$, e·Å$^{-3}$ | $H$, a.u. | $V$, a.u. | $G$, a.u. | $\eta$ | R(X-H---Y), Å |
|-------|-------------------|----------------------|-----------|-----------|-----------|--------|----------------|
| Compound I                      |                      |                      |           |           |           |        |                |
| 1     | 0.0294            | 0.1165               | −0.0147   | −0.0585   | 0.0438    | 0.2540 | 1.61           |
| 2     | 0.0155            | 0.0739               | −0.0011   | −0.0207   | 0.0196    | 0.1660 | 1.94           |
| 3     | 0.0201            | 0.1067               | −0.0037   | −0.0341   | 0.0304    | 0.1650 | 1.77           |
| 4     | 0.0265            | 0.1139               | −0.0112   | −0.0508   | 0.0397    | 0.2261 | 1.65           |
| 5     | 0.0070            | 0.0523               | 0.0027    | 0.0076    | 0.0103    | 0.0489 | 2.23           |
| 5*    | 0.0071            | 0.0527               | 0.0027    | −0.0077   | 0.0104    | 0.0493 | 2.23           |
| 6     | 0.0108            | 0.0619               | 0.0014    | −0.0127   | 0.0141    | 0.0619 | 2.09           |
| 7     | 0.0270            | 0.0845               | −0.0126   | −0.0464   | 0.0338    | 0.3011 | 1.70           |
| Compound II                     |                      |                      |           |           |           |        |                |
| 8     | 0.0295            | 0.1168               | −0.0148   | −0.0588   | 0.0440    | 0.2550 | 1.61           |
| 9     | 0.0296            | 0.1169               | −0.0148   | −0.0588   | 0.0440    | 0.2552 | 1.62           |
| 10    | 0.0200            | 0.1069               | −0.0037   | −0.0340   | 0.0304    | 0.1637 | 1.77           |
| 11    | 0.0275            | 0.0843               | −0.0132   | −0.0475   | 0.0343    | 0.3074 | 1.69           |

Note: 5* is for another position of O atoms.
to the absence of hydrogen bonding in compound III and
the presence of comparatively longer and weaker hydrogen
bonds between dimers in compound II compared with
compound I. The wide melting range for compound II
is possibly related to the intermolecular interactions with
participation of chlorine atoms.

CONCLUSIONS

Our study demonstrated that intermolecular
hydrogen bonding plays an important role in crystal
packing, molecule association, and self-organization,
and it explains some contradictions between the
theoretical data for the molecules in the gas phase
and experimental results for compounds in the solid
state. Differentiation was determined between strong
interactions due to participation of atoms with high
electronegativity (O, N) and the weak (dispersion)
one, the dimer formation being the first step of
extended species formation.

APPENDIX A

Supplementary data to this article can be found after this
article and online at https://doi.org/10.32362/2410-6593-2021-
16-2-113-124 (Supplementary files).
The authors were equally involved in the work on the article.
The authors declare no conflicts of interest.

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**Тонкие химические технологии = Fine Chemical Technologies. 2021;16(2):113–124**
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Edited for English language and spelling by Enago, an editing brand of Crimson Interactive Inc.

The text was submitted by the authors in English.

Edited for English language and spelling by Enago, an editing brand of Crimson Interactive Inc.
### Table A1. Crystal data and the details of data collection and refinement for compounds I, II, and III

| Compound | I | II | III |
|----------|---|----|-----|
| **Empirical formula** | C₁₀H₁₀N₂O | C₁₀H₁₂ClN₂O | C₁₁H₁₂N₂O |
| **Formula weight** | 174.20 | 208.64 | 188.23 |
| **Crystal system, Sp. gr., Z** | Monoclinic, P2₁/c, 8 | Triclinic, P–1, 2 | Monoclinic, C2/c, 8 |
| **a, b, c, Å** | a = 10.331(3) | a = 5.8551(12) | a = 16.892(9) |
| | b = 11.155(4) | b = 7.674(3) | b = 7.429(3) |
| | c = 15.880(5) | c = 11.348(3) | c = 17.776(8) |
| **α, β, γ, °; V, Å³** | 90.00, 95.06(3), 90.00; 1822.9 (10) | 106.11(2), 94.669(19), 101.51(2); 475.0(2) | 90.00, 116.98(5), 90.00; 1987.9(16) |
| **F(000)** | 736 | 216 | 800 |
| **Dₐ, Mg·m⁻³** | 1.269 | 1.459 | 1.258 |
| **Radiation** | Cu Kα radiation, λ = 1.5418 Å, Cell parameters from 25 reflections θ = 33°–35° | Cu Kα radiation, λ = 1.5418 Å, Cell parameters from 25 reflections θ = 30°–33° | Ag Kα radiation, λ = 0.56087 Å, Cell parameters from 25 reflections θ = 15°–16° |
| **μ, mm⁻¹** | 0.68 | 3.28 | 0.05 |
| **Crystal size, mm³** | 0.20 × 0.20 × 0.20 Colorless prisms | 0.10 × 0.10 × 0.10 Colorless prisms | 0.50 × 0.50 × 0.50 Colorless prisms |

Data collection: Enraf_Nonius CAD4 diffractometer³; radiation source: fine-focus sealed tube; monochromator: graphite; non–profiled o scans.

³ Enraf_Nonius CAD4 Software. Version 5.0. Delft (The Netherlands): Enraf_Nonius, 1989.
| H-atom treatment | H atoms were treated by a mixture of independent and constrained refinement | H-atom parameters constrained |
|------------------|--------------------------------------------------------------------------------|--------------------------------|
| \( R[F^2 > 2\sigma(F^2)] \) | 0.037 | 0.057 | 0.058 |
| \( wR(F^2) \) | 0.102 | 0.158 | 0.175 |
| \( S \) | 1.04 | 1.06 | 1.01 |
| Reflections/parameters/restraints | 3450/250/0 | 1952/128/0 | 4882/130/0 |
| \( \Delta \rho_{\text{max}}/\Delta \rho_{\text{min}} \) eÅ\(^{-3} \) | 0.15/−0.11 | 0.33/−0.22 | 0.26/−0.30 |

**Note:**
- \( Z \) = the number of formula units in the unit cell;
- \( R_w \) = merging error (measure of the precision/reproducibility);
- \( \theta_{\text{max}} \) = max \( \theta \) angle in degrees for the reflection used for measurement of the unit cell;
- \( \theta_{\text{min}} \) = min \( \theta \) angle in degrees for the reflection used for measurement of the unit cell;
- Sp. gr. = space group;
- \( \mu \) = absorption coefficient;
- \( \lambda \) = wavelength, refers to the radiation used to measure intensities;
- \( V \) = unit cell volume;
- \( a, b, \) and \( c \) = cell lengths; \( \alpha, \beta, \) and \( \gamma \) = cell angles;
- \( D \) = calculated density;
- \( I \) = intensity of reflection;
- \( R \) = R-factor;
- \( wR \) = weighed R-factor;
- \( F(000) \) = sum of all electrons in the unit cell;
- \( \sigma \) = standard deviation;
- \( S \) = goodness of fit;
- \( h, k, \) and \( l \) = Miller indices;
- \( I > 2\sigma(I) \) = criterion for strong reflections.
Table A2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for compound I

| Atom | x          | y          | z          | U¹ iso/√Ueq |
|------|------------|------------|------------|-------------|
| N1   | 0.19338 (10) | 0.37391 (8) | 0.06745 (7) | 0.0430 (2)  |
| N2   | 0.27022 (11) | 0.29948 (9) | 0.02385 (7) | 0.0498 (3)  |
| C3   | 0.32777 (14) | 0.37019 (11) | −0.02844 (9) | 0.0518 (3)  |
| C4   | 0.29077 (14) | 0.48962 (11) | −0.01909 (9) | 0.0530 (3)  |
| H4   | 0.3209 (16) | 0.5576 (15) | −0.0496 (10) | 0.067 (5)*  |
| C5   | 0.20504 (12) | 0.48922 (10) | 0.04174 (8)  | 0.0439 (3)  |
| O5   | 0.13825 (10) | 0.57503 (8) | 0.07625 (7)  | 0.0570 (3)  |
| H5   | 0.1924 (18) | 0.6493 (19) | 0.0784 (12)  | 0.087 (6)*  |
| C6   | 0.11839 (13) | 0.32597 (10) | 0.12979 (8)  | 0.0455 (3)  |
| C7   | −0.00259 (14) | 0.37340 (13) | 0.14200 (9)  | 0.0555 (3)  |
| H7   | −0.0347 | 0.4389 | 0.1105 | 0.067* |
| C8   | −0.07485 (17) | 0.32197 (17) | 0.20172 (12) | 0.0747 (5)  |
| H8   | −0.1553 | 0.3543 | 0.2110 | 0.090* |
| C9   | −0.0297 (2) | 0.22383 (18) | 0.24762 (12) | 0.0854 (6)  |
| H9   | −0.0802 | 0.1886 | 0.2865 | 0.102* |
| C10  | 0.0912 (2) | 0.17804 (15) | 0.23559 (11) | 0.0802 (6)  |
| H10  | 0.1224 | 0.1122 | 0.2670 | 0.096* |
| C11  | 0.16638 (17) | 0.22889 (12) | 0.17740 (9)  | 0.0598 (4)  |
| H11  | 0.2484 | 0.1984 | 0.1702 | 0.072* |
| C12  | 0.41644 (18) | 0.31848 (16) | −0.08831 (12) | 0.0780 (5)  |
| H12A | 0.5048 | 0.3378 | −0.0694 | 0.117* |
| H12B | 0.3954 | 0.3514 | −0.1437 | 0.117* |
| H12C | 0.4061 | 0.2330 | −0.0904 | 0.117* |
| N21  | 0.30234 (11) | 0.96602 (8) | 0.07065 (7)  | 0.0473 (3)  |
| N22  | 0.26333 (12) | 1.04936 (9) | 0.00912 (8)  | 0.0517 (3)  |
| H22  | 0.2696 (16) | 1.1302 (18) | 0.0200 (11)  | 0.075 (5)*  |
| C23  | 0.16953 (14) | 0.99970 (12) | −0.04340 (9) | 0.0546 (3)  |
| C24  | 0.15371 (15) | 0.88297 (12) | −0.02102 (10) | 0.0564 (4)  |
| H24  | 0.0945 (16) | 0.8289 (15) | −0.0484 (10) | 0.068 (5)*  |
| C25  | 0.23756 (13) | 0.85971 (10) | 0.05141 (9)  | 0.0486 (3)  |
| O25  | 0.26042 (11) | 0.76589 (8) | 0.09483 (7)  | 0.0646 (3)  |
| C26  | 0.41009 (12) | 0.98926 (10) | 0.12963 (9)  | 0.0468 (3)  |
| C27  | 0.42958 (16) | 0.92134 (13) | 0.20319 (10) | 0.0606 (4)  |
### Table A2. Continued

| Atom | \(x\)     | \(y\)     | \(z\)     | \(U_{\text{iso}}/U_{\text{eq}}\) |
|------|-----------|-----------|-----------|----------------------------------|
| H27  | 0.3720    | 0.8601    | 0.2137    | 0.073*                           |
| C28  | 0.53456 (18) | 0.94523 (17) | 0.26046 (11) | 0.0752 (5)                     |
| H28  | 0.5485    | 0.8987    | 0.3090    | 0.090*                           |
| C29  | 0.61888 (18) | 1.03716 (19) | 0.24653 (13) | 0.0799 (5)                     |
| H29  | 0.6887    | 1.0536    | 0.2859    | 0.096*                           |
| C30  | 0.59944 (16) | 1.10417 (17) | 0.17444 (13) | 0.0750 (5)                     |
| H30  | 0.6563    | 1.1665    | 0.1652    | 0.090*                           |
| C31  | 0.49607 (14) | 1.08054 (13) | 0.11487 (11) | 0.0595 (4)                     |
| H31  | 0.4847    | 1.1256    | 0.0655    | 0.071*                           |
| C32  | 0.10490 (19) | 1.07208 (16) | −0.11336 (11) | 0.0751 (5)                     |
| H32A | 0.0953    | 1.1532    | −0.0947   | 0.113*                           |
| H32B | 0.0208    | 1.0389    | −0.1301   | 0.113*                           |
| H32C | 0.1568    | 1.0710    | −0.1606   | 0.113*                           |

*Note:* The sign * indicates the isotropic displacement parameters, Å\(^2\).

### Table A3. Atomic displacement parameters (Å\(^2\)) for compound I

| Atom  | \(U_{11}\)      | \(U_{22}\)      | \(U_{33}\)      | \(U_{12}\)      | \(U_{13}\)      | \(U_{23}\)      |
|-------|------------------|------------------|------------------|-----------------|-----------------|-----------------|
| N1    | 0.0534 (6)       | 0.0206 (4)       | 0.0566 (6)       | −0.0024 (4)     | 0.0141 (5)      | −0.0016 (4)     |
| N2    | 0.0611 (7)       | 0.0248 (5)       | 0.0661 (7)       | 0.0017 (4)      | 0.0207 (5)      | −0.0021 (4)     |
| C3    | 0.0578 (7)       | 0.0343 (6)       | 0.0656 (8)       | −0.0016 (5)     | 0.0180 (6)      | 0.0004 (6)      |
| C4    | 0.0654 (8)       | 0.0278 (6)       | 0.0681 (8)       | −0.0062 (6)     | 0.0182 (7)      | 0.0068 (6)      |
| C5    | 0.0535 (7)       | 0.0206 (5)       | 0.0582 (7)       | −0.0031 (5)     | 0.0080 (6)      | −0.0013 (5)     |
| O5    | 0.0680 (6)       | 0.0238 (4)       | 0.0819 (7)       | −0.0005 (4)     | 0.0224 (5)      | −0.0055 (4)     |
| C6    | 0.0581 (7)       | 0.0275 (6)       | 0.0522 (7)       | −0.0118 (5)     | 0.0124 (6)      | −0.0068 (5)     |
| C7    | 0.0565 (8)       | 0.0460 (7)       | 0.0652 (8)       | −0.0128 (6)     | 0.0128 (6)      | −0.0136 (6)     |
| C8    | 0.0718 (10)      | 0.0743 (11)      | 0.0825 (11)      | −0.0306 (9)     | 0.0328 (9)      | −0.0272 (9)     |
| C9    | 0.1175 (16)      | 0.0750 (12)      | 0.0694 (10)      | −0.0501(12)     | 0.0415 (11)     | −0.0159 (9)     |
| C10   | 0.1320 (17)      | 0.0452 (9)       | 0.0659 (10)      | −0.0267(10)     | 0.0222 (10)     | 0.0051 (7)      |
| C11   | 0.0854 (10)      | 0.0328 (6)       | 0.0628 (8)       | −0.0065 (6)     | 0.0152 (7)      | 0.0018 (6)      |
| C12   | 0.0865 (12)      | 0.0592 (10)      | 0.0951 (12)      | 0.0037 (8)      | 0.0462 (10)     | −0.0027 (9)     |
| N21   | 0.0558 (6)       | 0.0203 (4)       | 0.0649 (6)       | −0.0015 (4)     | −0.0003 (5)     | −0.0005 (4)     |
| N22   | 0.0660 (7)       | 0.0233 (5)       | 0.0648 (7)       | −0.0013 (5)     | −0.0004 (6)     | −0.0012 (5)     |
| C23   | 0.0625 (8)       | 0.0395 (7)       | 0.0613 (8)       | 0.0002 (6)      | 0.0019 (6)      | −0.0059 (6)     |
| C24   | 0.0623 (8)       | 0.0363 (7)       | 0.0699 (9)       | −0.0102 (6)     | 0.0020 (7)      | −0.0121 (6)     |
Table A3. Continued

| Atom | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|------|------------|------------|------------|------------|------------|------------|
| C25  | 0.0540 (7) | 0.0220 (5) | 0.0707 (8) | −0.0033 (5)| 0.0099 (6) | −0.0068 (5)|
| O25  | 0.0771 (7) | 0.0234 (4) | 0.0925 (8) | −0.0051 (4)| 0.0027 (6) | 0.0034 (4) |
| C26  | 0.0497 (7) | 0.0283 (6) | 0.0626 (7) | 0.0039 (5) | 0.0064 (6) | −0.0092 (5)|
| C27  | 0.0675 (9) | 0.0459 (8) | 0.0683 (9) | 0.0036 (7) | 0.0058 (7) | 0.0002 (7) |
| C28  | 0.0793 (11)| 0.0766 (11)| 0.0676 (10)| 0.0117 (9) | −0.0046 (8)| −0.0029 (8)|
| C29  | 0.0662 (10)| 0.0902 (13)| 0.0802 (11)| 0.0004 (10)| −0.0099 (9)| −0.0195 (10)|
| C30  | 0.0607 (9) | 0.0674 (10)| 0.0966 (13)| −0.0145 (8)| 0.0047 (9) | −0.0190 (10)|
| C31  | 0.0587 (8) | 0.0446 (7) | 0.0749 (9) | −0.0085 (6)| 0.0050 (7) | −0.0059 (7)|
| C32  | 0.0907 (12)| 0.0627 (10)| 0.0691 (10)| 0.0040 (9) | −0.0079 (9)| 0.0032 (8) |

Table A4. Geometric parameters (Å, °) for compound I

| Atom–Atom | Bond length, Å | Atom–Atom | Bond length, Å |
|-----------|---------------|-----------|---------------|
| N1–C5     | 1.3581 (15)   | N21–C25   | 1.3826 (15)   |
| N1–N2     | 1.3768 (14)   | N21–N22   | 1.3827 (15)   |
| N1–C6     | 1.4147 (16)   | N21–C26   | 1.4140 (18)   |
| N2–C3     | 1.3237 (17)   | N22–C23   | 1.3413 (19)   |
| C3–C4     | 1.3976 (18)   | N22–H22   | 0.92 (2)      |
| C3–C12    | 1.493 (2)     | C23–C24   | 1.363 (2)     |
| C4–C5     | 1.367 (2)     | C23–C32   | 1.484 (2)     |
| C4–H4     | 0.966 (17)    | C24–C25   | 1.402 (2)     |
| C5–O5     | 1.3265 (15)   | C24–H24   | 0.938 (17)    |
| O5–H5     | 1.00 (2)      | C25–O25   | 1.2640 (16)   |
| C6–C7     | 1.386 (2)     | C26–C31   | 1.3848 (19)   |
| C6–C11    | 1.3870 (19)   | C26–C27   | 1.392 (2)     |
| C7–C8     | 1.382 (2)     | C27–C28   | 1.379 (2)     |
| C7–H7     | 0.9300        | C27–H27   | 0.9300        |
| C8–C9     | 1.374 (3)     | C28–C29   | 1.376 (3)     |
| C8–H8     | 0.9300        | C28–H28   | 0.9300        |
| C9–C10    | 1.378 (3)     | C29–C30   | 1.367 (3)     |
| C9–H9     | 0.9300        | C29–H29   | 0.9300        |
| C10–C11   | 1.381 (2)     | C30–C31   | 1.388 (2)     |
| C10–H10   | 0.9300        | C30–H30   | 0.9300        |
| C11–H11   | 0.9300        | C31–H31   | 0.9300        |
| C12–H12A  | 0.9600        | C32–H32A  | 0.9600        |
| C12–H12B  | 0.9600        | C32–H32B  | 0.9600        |
| C12–H12C  | 0.9600        | C32–H32C  | 0.9600        |
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Table A4. Continued

| Angle         | Angle value, ° | Angle         | Angle value, ° |
|---------------|----------------|---------------|----------------|
| C5–N1–N2     | 110.46 (10)    | C25–N21–C26  | 129.87 (10)    |
| C5–N1–C6     | 129.57 (10)    | N22–N21–C26  | 120.54 (10)    |
| N2–N1–C6     | 119.97 (9)     | C23–N22–N21  | 108.14 (11)    |
| C3–N2–N1     | 105.48 (10)    | C23–N22–H22  | 123.9 (11)     |
| N2–C3–C4     | 111.05 (12)    | N21–N22–H22  | 121.0 (11)     |
| N2–C3–C12    | 120.26 (12)    | N22–C23–C24  | 109.21 (13)    |
| C4–C3–C12    | 128.67 (13)    | N22–C23–C32  | 119.58 (13)    |
| C5–C4–C3     | 105.80 (11)    | C24–C23–C32  | 131.20 (14)    |
| C5–C4–H4     | 127.9 (10)     | C23–C24–C25  | 108.13 (12)    |
| C3–C4–H4     | 126.3 (10)     | C23–C24–H24  | 125.5 (10)     |
| O5–C5–N1     | 119.74 (11)    | C25–C24–H24  | 126.3 (10)     |
| O5–C5–C4     | 133.05 (11)    | O25–C25–N21  | 121.75 (13)    |
| N1–C5–C4     | 107.21 (10)    | O25–C25–C24  | 132.31 (12)    |
| C5–O5–H5     | 107.6 (11)     | N21–C25–C24  | 105.94 (11)    |
| C7–C6–C11    | 120.33 (13)    | C31–C26–C27  | 119.65 (14)    |
| C7–C6–N1     | 120.64 (12)    | C31–C26–N21  | 120.13 (13)    |
| C11–C6–N1    | 119.01 (12)    | C27–C26–N21  | 120.21 (12)    |
| C8–C7–C6     | 119.05 (16)    | C28–C27–C26  | 119.71 (15)    |
| C8–C7–H7     | 120.5          | C28–C27–H27  | 120.1          |
| C6–C7–H7     | 120.5          | C26–C27–H27  | 120.1          |
| C9–C8–C7     | 121.06 (17)    | C29–C28–C27  | 120.69 (17)    |
| C9–C8–H8     | 119.5          | C29–C28–H28  | 119.7          |
| C7–C8–H8     | 119.5          | C27–C28–H28  | 119.7          |
| C8–C9–C10    | 119.44 (15)    | C30–C29–C28  | 119.59 (16)    |
| C8–C9–H9     | 120.3          | C30–C29–H29  | 120.2          |
| C10–C9–H9    | 120.3          | C28–C29–H29  | 120.2          |
| C9–C10–C11   | 120.72 (18)    | C29–C30–C31  | 120.95 (17)    |
| C9–C10–H10   | 119.6          | C29–C30–H30  | 119.5          |
| C11–C10–H10  | 119.6          | C31–C30–H30  | 119.5          |
| C10–C11–C6   | 119.37 (16)    | C26–C31–C30  | 119.39 (16)    |
| C10–C11–H11  | 120.3          | C26–C31–H31  | 120.3          |
| C6–C11–H11   | 120.3          | C30–C31–H31  | 120.3          |
| C3–C12–H12A  | 109.5          | C23–C32–H32A | 109.5          |
| C3–C12–H12B  | 109.5          | C23–C32–H32B | 109.5          |
| H12A–C12–H12B| 109.5          | H32A–C32–H32B| 109.5          |
| Torsion angle | Angle value, ° | Torsion angle | Angle value, ° |
|---------------|---------------|---------------|---------------|
| C5–N1–N2–C3  | −0.26 (15)    | C5–N1–N2–C3  | 4.61 (15)     |
| C6–N1–N2–C3  | −179.50 (12)  | C6–N1–N2–C3  | 4.61 (12)     |
| N1–N2–C3–C4  | 0.60 (16)     | N1–N2–C3–C4  | −4.54 (16)    |
| N1–N2–C3–C12 | −178.10 (14)  | N1–N2–C3–C12 | 176.90 (14)   |
| N2–C3–C4–C5  | −0.72 (18)    | N2–C3–C4–C5  | 2.76 (17)     |
| C12–C3–C4–C5 | 177.84 (16)   | C12–C3–C4–C5 | −178.91 (16)  |
| C2–N1–C5–O5  | 179.90 (11)   | C2–N1–C5–O5  | 175.97 (13)   |
| C6–N1–C5–O5  | −0.9 (2)      | C6–N1–C5–O5  | 8.8 (2)       |
| N2–N1–C5–C4  | −0.18 (15)    | N2–N1–C5–C4  | −2.85 (15)    |
| C6–N1–C5–C4  | 178.97 (13)   | C6–N1–C5–C4  | −170.05 (13)  |
| C3–C4–C5–O5  | −179.57 (15)  | C3–C4–C5–O5  | −178.53 (16)  |
| C3–C4–C5–N1  | 0.52 (16)     | C3–C4–C5–N1  | 0.12 (16)     |
| C5–N1–C6–C7  | 35.6 (2)      | C5–N1–C6–C7  | 150.33 (14)   |
| N2–N1–C6–C7  | −145.28 (12)  | N2–N1–C6–C7  | −15.54 (18)   |
| C5–N1–C6–C11 | −145.78 (14)  | C5–N1–C6–C11 | −30.3 (2)     |
| N2–N1–C6–C11 | 33.30 (17)    | N2–N1–C6–C11 | 163.82 (12)   |
| C11–C6–C7–C8 | −0.5 (2)      | C11–C6–C7–C8 | −0.3 (2)      |
| N1–C6–C7–C8  | 178.05 (12)   | N1–C6–C7–C8  | −179.65 (13)  |
| C6–C7–C8–C9  | −1.2 (2)      | C6–C7–C8–C9  | 1.3 (2)       |
| C7–C8–C9–C10 | 1.8 (3)       | C7–C8–C9–C10 | −1.1 (3)      |
| C8–C9–C10–C11| −0.7 (3)      | C8–C9–C10–C11| −0.3 (3)      |
| C9–C10–C11–C6| −1.0 (2)      | C9–C10–C11–C6| −1.0 (2)      |
| C7–C6–C11–C10| 1.6 (2)       | C7–C6–C11–C10| 178.35 (13)   |
| N1–C6–C11–C10| −176.98 (13)  | N1–C6–C11–C10| 1.3 (3)       |

Hydrogen-bond geometry (Å, º)

| D–H---A       | D–H   | H---A | D---A   | D–H---A |
|---------------|-------|-------|---------|---------|
| O5–H5---O25   | 1.00 (2) | 1.49 (2) | 2.4794 (14) | 169.8 (18) |
| N22–H22---N2' | 0.92 (2) | 1.89 (2) | 2.8004 (17) | 170.5 (16) |

Symmetry code: (i) x, y + 1, z.
### Table A5. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for compound II

| Atom  | \(x\)       | \(y\)       | \(z\)       | \(U_{iso}^{\#}\) | \(U_{eq}\)  |
|-------|--------------|--------------|--------------|-------------------|-------------|
| Cl1   | 0.03028 (10) | 0.54630 (7)  | 0.35235 (4)  | 0.0752 (3)        |             |
| N1    | −0.0218 (2)  | 0.11695 (18) | −0.17303 (11)| 0.0448 (3)        |             |
| N2    | −0.2362 (2)  | 0.00890 (18) | −0.23953 (12)| 0.0491 (3)        |             |
| H2    | −0.3709      | 0.0045       | −0.2140      | 0.059*            |             |
| C3    | −0.1961 (3)  | −0.0883 (2)  | −0.35162 (15)| 0.0510 (4)        |             |
| C4    | 0.0361 (3)   | −0.0560 (2)  | −0.35717 (15)| 0.0510 (4)        |             |
| H4    | 0.1068       | −0.1099      | −0.4241      | 0.061*            |             |
| C5    | 0.1557 (2)   | 0.0752 (2)   | −0.24282 (14)| 0.0487 (4)        |             |
| O5    | 0.36892 (19) | 0.14357 (19) | −0.20424 (12)| 0.0616 (4)        |             |
| Cl2   | −0.3968 (3)  | −0.2094 (3)  | −0.44703 (18)| 0.0706 (5)        |             |
| H12A  | −0.5131      | −0.2709      | −0.4079      | 0.106*            |             |
| H12B  | −0.3411      | −0.3009      | −0.5067      | 0.106*            |             |
| H12C  | −0.4657      | −0.1344      | −0.4881      | 0.106*            |             |
| C6    | −0.0052 (2)  | 0.21556 (19) | −0.04676 (13)| 0.0431 (3)        |             |
| C7    | 0.1996 (3)   | 0.3438 (2)   | 0.01551 (16) | 0.0532 (4)        |             |
| H7    | 0.3290       | 0.3629       | −0.0256      | 0.064*            |             |
| C8    | 0.2129 (3)   | 0.4441 (3)   | 0.13892 (17) | 0.0579 (4)        |             |
| H8    | 0.3511       | 0.5290       | 0.1816       | 0.070*            |             |
| C9    | 0.0174 (3)   | 0.4155 (2)   | 0.19710 (15) | 0.0544 (4)        |             |
| C10   | −0.1861 (3)  | 0.2891 (3)   | 0.13769 (15) | 0.0565 (4)        |             |
| H10   | −0.3152      | 0.2717       | 0.1793       | 0.068*            |             |
| C11   | −0.1989 (3)  | 0.1865 (2)   | 0.01432 (14) | 0.0520 (4)        |             |
| H11   | −0.3361      | 0.0990       | −0.0270      | 0.062*            |             |

*Note:* The sign * indicates the isotropic displacement parameters, Å².

### Table A6. Atomic displacement parameters (Å²) for compound II

| Atom  | \(U^{11}\) | \(U^{22}\) | \(U^{33}\) | \(U^{12}\) | \(U^{13}\) | \(U^{23}\) |
|-------|------------|------------|------------|------------|------------|------------|
| Cl1   | 0.0948 (5) | 0.0763 (4) | 0.0413 (3) | 0.0189 (3) | 0.0047 (3) | −0.0013 (2) |
| N1    | 0.0331 (6) | 0.0553 (7) | 0.0374 (6) | 0.0073 (5) | 0.0003 (5) | 0.0038 (5)  |
| N2    | 0.0356 (6) | 0.0574 (7) | 0.0438 (7) | 0.0084 (5) | −0.0002 (5)| 0.0019 (6)  |
| C3    | 0.0473 (8) | 0.0519 (8) | 0.0433 (8) | 0.0116 (6) | −0.0036 (6)| 0.0002 (6)  |
| C4    | 0.0460 (8) | 0.0585 (8) | 0.0416 (8) | 0.0166 (6) | 0.0047 (6) | 0.0015 (6)  |
| C5    | 0.0395 (7) | 0.0617 (8) | 0.0426 (8) | 0.0147 (6) | 0.0049 (6) | 0.0104 (7)  |
Table A6. Continued

| Atom  | $U^{31}$  | $U^{32}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| O5    | 0.0345 (5) | 0.0772 (8) | 0.0577 (7) | 0.0102 (5) | 0.0046 (5) | −0.0020 (6) |
| C12   | 0.0497 (9) | 0.0786 (11) | 0.0591 (11) | 0.0118 (9) | −0.0054 (8) | −0.0125 (9) |
| C6    | 0.0418 (8) | 0.0480 (7) | 0.0350 (7) | 0.0106 (6) | −0.0007 (5) | 0.0072 (6) |
| C7    | 0.0411 (7) | 0.0565 (8) | 0.0490 (8) | 0.0044 (6) | 0.0035 (6) | 0.0010 (7) |
| C8    | 0.0499 (9) | 0.0589 (9) | 0.0505 (9) | 0.0031 (7) | −0.0035 (7) | 0.0028 (7) |
| C9    | 0.0633 (10) | 0.0550 (8) | 0.0410 (8) | 0.0165 (7) | −0.0005 (7) | 0.0085 (7) |
| C10   | 0.0531 (9) | 0.0723 (10) | 0.0408 (8) | 0.0107 (7) | 0.0099 (6) | 0.0137 (7) |
| C11   | 0.0432 (8) | 0.0629 (9) | 0.0401 (8) | 0.0023 (6) | 0.0006 (6) | 0.0084 (7) |

Table A7. Geometric parameters (Å, °) for compound II

| Atom–Atom | Bond length, Å | Atom–Atom | Bond length, Å |
|-----------|----------------|-----------|----------------|
| C11–C9    | 1.7562 (18)    | C12–H12B  | 0.9600         |
| N1–N2     | 1.3843 (17)    | C12–H12C  | 0.9600         |
| N1–C5     | 1.3914 (17)    | C6–C7     | 1.382 (2)      |
| N1–C6     | 1.4077 (18)    | C6–C11    | 1.389 (2)      |
| N2–C3     | 1.349 (2)      | C7–C8     | 1.385 (2)      |
| N2–H2     | 0.8600         | C7–H7     | 0.9300         |
| C3–C4     | 1.343 (2)      | C8–C9     | 1.377 (2)      |
| C3–C12    | 1.488 (2)      | C8–H8     | 0.9300         |
| C4–C5     | 1.426 (2)      | C9–C10    | 1.364 (3)      |
| C4–H4     | 0.9300         | C10–C11   | 1.391 (2)      |
| C5–O5     | 1.2440 (19)    | C10–H10   | 0.9300         |
| C12–H12A  | 0.9600         | C11–H11   | 0.9300         |

| Angle     | Angle value, ° | Angle     | Angle value, ° |
|-----------|----------------|-----------|----------------|
| N2–N1–C5 | 108.65 (12)    | H12B–C12–H12C | 109.5 |
| N2–N1–C6 | 120.36 (12)    | C7–C6–C11  | 120.05 (14)    |
| C5–N1–C6 | 129.59 (12)    | C7–C6–N1   | 120.55 (13)    |
| C3–N2–N1 | 107.82 (12)    | C11–C6–N1  | 119.38 (13)    |
| C3–N2–H2 | 126.1          | C6–C7–C8   | 120.31 (15)    |
| N1–N2–H2 | 126.1          | C6–C7–H7   | 119.8          |
| C4–C3–N2 | 110.05 (15)    | C8–C7–H7   | 119.8          |
| C4–C3–C12| 129.74 (16)    | C9–C8–C7   | 118.70 (16)    |
| N2–C3–C12| 120.20 (15)    | C9–C8–H8   | 120.6          |
### Table A7. Continued

| Torsion angle       | Angle value, ° | Torsion angle       | Angle value, ° |
|---------------------|----------------|---------------------|----------------|
| C5–N1–N2–C3         | −4.19 (17)     | C5–N1–C6–C7         | 24.4 (2)       |
| C6–N1–N2–C3         | −171.92 (12)   | N2–N1–C6–C11        | 7.6 (2)        |
| N1–N2–C3–C4         | 3.76 (19)      | C5–N1–C6–C11        | −157.28 (15)   |
| N1–N2–C3–C12        | −176.41 (16)   | C11–C6–C7–C8        | 0.0 (3)        |
| N2–C3–C4–C5         | −1.88 (19)     | N1–C6–C7–C8         | 178.29 (13)    |
| C12–C3–C4–C5        | 178.31 (19)    | C6–C7–C8–C9         | −1.1 (3)       |
| N2–N1–C5–O5         | −176.12 (15)   | C7–C8–C9–C10        | 1.4 (3)        |
| C6–N1–C5–O5         | −9.9 (3)       | C7–C8–C9–C11        | −178.39 (12)   |
| N2–N1–C5–C4         | 2.98 (16)      | C8–C9–C10–C11       | −0.6 (3)       |
| C6–N1–C5–C4         | 169.22 (14)    | C11–C9–C10–C11      | 179.25 (12)    |
| C3–C4–C5–O5         | 178.28 (18)    | C7–C6–C11–C10       | 0.9 (2)        |
| C3–C4–C5–N1         | −0.72 (17)     | N1–C6–C11–C10       | −177.44 (14)   |
| N2–N1–C6–C7         | −170.78 (13)   | C9–C10–C11–C6       | −0.6 (3)       |

Hydrogen-bond geometry (Å, °)

| D–H---A             | D–H | H---A | D---A | D–H---A |
|---------------------|-----|-------|-------|---------|
| N2–H2---O5          | 0.86| 2.02  | 2.7293 (18) | 139 |

Symmetry code: (i) x–1, y, z.

### Table A8. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for compound III

| Atom | x       | y        | z        | U iso */*U eq |
|------|---------|----------|----------|--------------|
| N1   | 0.48507 (6) | 0.37211 (12) | 0.10131 (6) | 0.0388 (2) |
| N2   | 0.47599 (6) | 0.54096 (11) | 0.13277 (6) | 0.0393 (2) |
### Table A8. Continued

| Atom | $x$ | $y$ | $z$ | $U_{\text{eq}} / U_{eq}$ |
|------|-----|-----|-----|--------------------------|
| C3   | 0.38667 (7) | 0.58089 (15) | 0.09304 (7) | 0.0399 (2) |
| C4   | 0.33980 (7) | 0.43974 (16) | 0.04683 (7) | 0.0432 (3) |
| H4   | 0.2783 | 0.4342 | 0.0164 | 0.052* |
| O4   | 0.38798 (6) | 0.14436 (13) | 0.02542 (6) | 0.0562 (3) |
| C5   | 0.40039 (7) | 0.29940 (16) | 0.05233 (7) | 0.0397 (2) |
| C6   | 0.56111 (6) | 0.26616 (14) | 0.15091 (7) | 0.0357 (2) |
| C7   | 0.59414 (8) | 0.14975 (16) | 0.11065 (8) | 0.0445 (3) |
| H7   | 0.5680 | 0.1449 | 0.0520 | 0.053* |
| C8   | 0.66604 (8) | 0.04131 (17) | 0.15833 (9) | 0.0490 (3) |
| H8   | 0.6882 | −0.0366 | 0.1315 | 0.059* |
| C9   | 0.70529 (8) | 0.04735 (17) | 0.24529 (8) | 0.0475 (3) |
| H9   | 0.7532 | −0.0271 | 0.2769 | 0.057* |
| C10  | 0.67305 (8) | 0.16467 (17) | 0.28522 (8) | 0.0451 (3) |
| H10  | 0.6998 | 0.1699 | 0.3439 | 0.054* |
| C11  | 0.60106 (7) | 0.27459 (16) | 0.23843 (7) | 0.0403 (2) |
| H11  | 0.5796 | 0.3536 | 0.2655 | 0.048* |
| C12  | 0.35505 (11) | 0.75872 (19) | 0.10678 (10) | 0.0607 (4) |
| H12A | 0.3672 | 0.8489 | 0.0747 | 0.091* |
| H12B | 0.3853 | 0.7889 | 0.1657 | 0.091* |
| H12C | 0.2923 | 0.7533 | 0.0888 | 0.091* |
| C13  | 0.54237 (9) | 0.67445 (18) | 0.14061 (10) | 0.0563 (3) |
| H13A | 0.5435 | 0.6874 | 0.0874 | 0.085* |
| H13B | 0.5997 | 0.6361 | 0.1827 | 0.085* |
| H13C | 0.5277 | 0.7879 | 0.1569 | 0.085* |

*Note:* The sign * indicates the isotropic displacement parameters, Å$^2$.

### Table A9. Atomic displacement parameters (Å$^2$) for compound III

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|------|---------|---------|---------|---------|---------|---------|
| N1   | 0.0333 (4) | 0.0354 (4) | 0.0417 (4) | −0.0002 (3) | 0.0118 (3) | −0.0046 (3) |
| N2   | 0.0368 (4) | 0.0299 (4) | 0.0447 (5) | −0.0007 (3) | 0.0129 (4) | −0.0017 (3) |
| C3   | 0.0398 (5) | 0.0369 (5) | 0.0389 (5) | 0.0063 (4) | 0.0142 (4) | 0.0074 (4) |
| C4   | 0.0340 (5) | 0.0439 (6) | 0.0433 (5) | 0.0023 (4) | 0.0102 (4) | 0.0036 (4) |
| O4   | 0.0471 (5) | 0.0474 (5) | 0.0614 (5) | −0.0062 (4) | 0.0135 (4) | −0.0189 (4) |
| C5   | 0.0352 (5) | 0.0420 (5) | 0.0360 (5) | −0.0028 (4) | 0.0109 (4) | −0.0027 (4) |
### Table A9. Continued

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| C6   | 0.0303 (4) | 0.0341 (4) | 0.0421 (5) | −0.0017 (3) | 0.0159 (4) | −0.0018 (4) |
| C7   | 0.0435 (6) | 0.0450 (6) | 0.0456 (6) | 0.0011 (5) | 0.0209 (5) | −0.0071 (5) |
| C8   | 0.0429 (6) | 0.0436 (6) | 0.0635 (7) | 0.0030 (5) | 0.0268 (5) | −0.0089 (5) |
| C9   | 0.0347 (5) | 0.0413 (6) | 0.0628 (7) | 0.0033 (4) | 0.0190 (5) | 0.0029 (5) |
| C10  | 0.0384 (5) | 0.0489 (6) | 0.0437 (5) | 0.0019 (5) | 0.0148 (4) | 0.0031 (5) |
| C11  | 0.0364 (5) | 0.0442 (5) | 0.0415 (5) | 0.0019 (4) | 0.0186 (4) | −0.0027 (4) |
| C12  | 0.0625 (8) | 0.0443 (7) | 0.0662 (8) | 0.0174 (6) | 0.0212 (7) | 0.0044 (6) |
| C13  | 0.0495 (7) | 0.0408 (6) | 0.0707 (8) | −0.0107 (5) | 0.0202 (6) | 0.0001 (6) |

### Table A10. Geometric parameters (Å, °) for compound III

| Atom–Atom | Bond length, Å | Atom–Atom | Bond length, Å |
|-----------|----------------|-----------|----------------|
| N1–C5     | 1.4021 (16)    | C8–C9     | 1.379 (2)      |
| N1–N2     | 1.4098 (13)    | C8–H8     | 0.9300         |
| N1–C6     | 1.4210 (16)    | C9–C10    | 1.3823 (18)    |
| N2–C3     | 1.3770 (17)    | C9–H9     | 0.9300         |
| N2–C13    | 1.4554 (16)    | C10–C11   | 1.3854 (18)    |
| C3–C4     | 1.3457 (17)    | C10–H10   | 0.9300         |
| C3–C12    | 1.4860 (18)    | C11–H11   | 0.9300         |
| C4–C5     | 1.4329 (17)    | C12–H12A  | 0.9600         |
| C4–H4     | 0.9300         | C12–H12B  | 0.9600         |
| O4–C5     | 1.2281 (15)    | C12–H12C  | 0.9600         |
| C6–C11    | 1.3883 (17)    | C13–H13A  | 0.9600         |
| C6–C7     | 1.3904 (15)    | C13–H13B  | 0.9600         |
| C7–H7     | 0.9300         | –         | –              |

| Angle   | Angle value, ° | Angle   | Angle value, ° |
|---------|----------------|---------|----------------|
| N1–N2–C5 | 108.98 (9)    | C5–N1–N2 | 119.6          |
| N1–C6–N2 | 123.53 (10)   | C5–C6–N2 | 119.68 (11)    |
| N2–C6–N1 | 118.50 (9)    | C6–N2–C6 | 120.2          |
| C3–N2–C13 | 106.22 (9)   | C3–C2–C13 | 120.2          |
| C3–C2–N1 | 121.31 (10)   | C3–N1–C2 | 120.42 (12)    |
| N1–N2–C13 | 115.25 (10)  | C1–N1–C2 | 119.8          |
| C4–C3–N2 | 110.46 (11)   | C1–C4–C3 | 119.8          |
Table A10. Continued

|   |   |   |   |
|---|---|---|---|
| C4–C3–C12 | 129.58 (12) | C10–C11–C6 | 119.61 (11) |
| N2–C3–C12 | 119.94 (11) | C10–C11–H11 | 120.2 |
| C3–C4–C5 | 108.73 (11) | C6–C11–H11 | 120.2 |
| C3–C4–H4 | 125.6 | C3–C12–H12A | 109.5 |
| C5–C4–H4 | 125.6 | C3–C12–H12B | 109.5 |
| O4–C5–N1 | 123.29 (11) | H12A–C12–H12B | 109.5 |
| O4–C5–C4 | 131.71 (11) | C3–C12–H12C | 109.5 |
| N1–C5–C4 | 104.94 (10) | H12A–C12–H12C | 109.5 |
| C11–C6–C7 | 120.02 (10) | H12B–C12–H12C | 109.5 |
| C11–C6–N1 | 120.88 (10) | N2–C13–H13A | 109.5 |
| C7–C6–N1 | 119.08 (10) | N2–C13–H13B | 109.5 |
| C8–C7–C6 | 119.56 (12) | H13A–C13–H13B | 109.5 |
| C8–C7–H7 | 120.2 | N2–C13–H13C | 109.5 |
| C6–C7–H7 | 120.2 | H13A–C13–H13C | 109.5 |
| C9–C8–C7 | 120.70 (11) | H13B–C13–H13C | 109.5 |
| C9–C8–H8 | 119.6 | – | – |

| Torsion angle | Angle value, ° | Torsion angle | Angle value, ° |
|---------------|---------------|---------------|---------------|
| C5–N1–N2–C3  | −8.50 (11)    | C3–C4–C5–O4  | 174.74 (13)   |
| C6–N1–N2–C3  | −156.86 (9)   | C3–C4–C5–N1  | −2.69 (13)    |
| C5–N1–N2–C13 | −145.85 (11)  | C5–N1–C6–C11 | −112.19 (12)  |
| C6–N1–N2–C13 | 65.80 (14)    | N2–N1–C6–C11 | 31.29 (14)    |
| N1–N2–C3–C4  | 6.83 (12)     | C5–N1–C6–C7  | 66.27 (14)    |
| C13–N2–C3–C4 | 141.00 (12)   | N2–N1–C6–C7  | −150.25 (10)  |
| N1–N2–C3–C12 | −174.78 (10)  | C11–C6–C7–C8 | 0.83 (17)     |
| C13–N2–C3–C12 | −40.61 (17)   | N1–C6–C7–C8  | −177.64 (11)  |
| N2–C3–C4–C5  | −2.62 (13)    | C6–C7–C8–C9  | 0.02 (18)     |
| C12–C3–C4–C5 | 179.20 (12)   | C7–C8–C9–C10 | −0.78 (19)    |
| N2–N1–C5–O4  | −170.83 (11)  | C8–C9–C10–C11 | 0.70 (18)  |
| C6–N1–C5–O4  | −24.42 (17)   | C9–C10–C11–C6 | 0.15 (18)  |
| N2–N1–C5–C4  | 6.87 (11)     | C7–C6–C11–C10 | −0.91 (17)  |
| C6–N1–C5–C4  | 153.29 (10)   | N1–C6–C11–C10 | 177.53 (10)  |