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Two tautomers in one crystal: 4(5)-nitro-5(4)-methoxyimidazole

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The case of prototropic annular tautomerism in an imidazole derivative has been found. The crystal structure contains a 50:50 mixture of two tautomers: 4-nitro-5-methoxyimidazole and 5-nitro-4-methoxyimidazole. The X-ray experiment actually shows the superposition of these compounds; it appears as if the structure is centrosymmetric and the N—H hydrogen atoms are disordered over two ring N atoms. Owing to the hydrogen-bond pattern, the values of their site occupation factors have to be exactly equal to 1/2. The molecules are connected into a three-dimensional network by means of N—H···N and C—H···O hydrogen bonds.

1. Introduction

Tautomerism occurs when two or more constitutional isomers of different connectivity exist in a dynamic equilibrium with each other (*e.g.* Katritzky *et al.*, 1991; Katritzky, 1995). The most frequently occurring case of tautomerism, prototropic tautomerism, involves a transfer of a proton from one position in a molecule to another. For cyclic compounds, the H atom can be exchanged between ring atoms (annular tautomerism) or between a ring and side-chain atoms (side-chain tautomerism).

The structural aspects of annular tautomerism in azoles have been widely discussed, especially for pyrazoles (Halcrow *et al.*, 1996; Llamas-Saiz *et al.*, 1999; Foces-Foces *et al.*, 2000). The annular tautomerism in diazoles is caused by the exchange of an H atom between different N atoms in the azole ring. In general, three different situations have been identified in the solid state (Foces-Foces *et al.*, 2000).

(i) Only the most stable tautomeric form of the molecule is observed in the crystal because the steric demands of the space-group symmetry prevent the interconversion of the tautomers. The (rare) cases of desmotropy, *i.e.* the crystallizing of different tautomers in different crystal forms, also fall into this category (for detailed discussion see, for example, García *et al.*, 2002). However, in principle and in reality there is a possibility of the existence of two tautomeric forms in the same crystal. Two arrangements are possible, yet they do not necessarily exclude each other: the tautomers either

(ii) can occupy distinct sites or

(iii) N—H hydrogen atoms can appear disordered.

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Table 1
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	$C_4H_5N_3O_3$	$C_4H_5N_3O_3$
M_r	143.11	143.11
Cell setting, space group	Monoclinic, *C*2/*c*	Monoclinic, *Cc*
a, *b*, *c* (Å)	7.5542 (6), 11.3112 (9), 13.4773 (10)	7.5542 (6), 11.3112 (9), 13.4773 (10)
β (°)	95.920 (6)	95.920 (6)
V (Å^3)	1145.45 (15)	1145.45 (15)
Z	8	8
D_x (Mg m^{-3})	1.660	1.660
Radiation type	Mo *K*α	Mo *K*α
No. of reflections for cell parameters	4048	4048
θ range (°)	4–22	4–22
μ (mm^{-1})	0.14	0.14
Temperature (K)	90 (1)	90 (1)
Crystal form, color	Prism, colorless	Prism, colorless
Crystal size (mm)	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.1
Data collection		
Diffractometer	KUMA KM4CCD four-circle	KUMA KM4CCD four-circle
Data collection method	ω scan	ω scan
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
$T_{\min}$	0.983	0.983
$T_{\max}$	0.984	0.984
No. of measured, independent and observed reflections	7556, 1513, 1266	7556, 2380, 1876
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.030	0.030
$\theta_{\max}$ (°)	29.0	29.9
Range of *h*, *k*, *l*	$-10 \Rightarrow h \Rightarrow 7$ $-15 \Rightarrow k \Rightarrow 15$ $-17 \Rightarrow l \Rightarrow 18$	$-10 \Rightarrow h \Rightarrow 7$ $-15 \Rightarrow k \Rightarrow 15$ $-17 \Rightarrow l \Rightarrow 18$
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.031, 0.080, 1.10	0.029, 0.074, 1.06
No. of reflections	1567	2380
No. of parameters	115	193
H-atom treatment	Refined independently	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.0996P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.043P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	<0.0001	0.120
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.26, −0.26	0.22, −0.26

Computer programs used: *CrysAlisCCD*, *SHELXS*97 (Sheldrick, 1990), *SHELXL*97 (Sheldrick, 1997).

As the hydrogen positions obtained from X-ray analysis might sometimes be questionable, Gdaniec *et al.* (1995) stressed the importance of hydrogen-bond patterns in corroborating the existence of different tautomers in the crystal.

Of course, the same three situations are in principle possible for imidazoles as well. Tautomerism of imidazole derivatives is especially interesting because of its biological importance. For example, tautomerism of biogenic amine histamine (2-aminoethylimidazole) plays an important role in the mechanism of activation for the H2 receptor (Topiol *et al.*, 1984; Worth *et al.*, 1990).

There are only a few examples of imidazole derivatives that have different tautomers in the solid state. In the CSD (Allen, 2002) there are 191 imidazole derivatives that could have different annular prototropic tautomers, including 4,5-dihydro modifications (only organic compounds, with no fused rings, coordinates available and duplicate entries excluded). In 74 of them (*ca* 39%) the hydrogen-bond pattern includes the N—H···N intermolecular bonds and therefore, in principle, two annular tautomers can make hydrogen-bonded chains. This possibility is realised only in a handful of structures, and most of them belong to category (ii): 5(4)-(3,3-dimethyl-1-triazenyl)imidazole-4-carboxamide (Freeman & Hutchinson, 1979) crystallizes in the space group $P2_1/n$ with eight molecules in the unit cell (Z' = 2); *N*-(4-chlorobenzylidene)-2-(4(5)imidazolyl)ethylamine (Bocelli & Cantoni, 1992), space group $P\bar{1}$, Z = 4 (Z' = 2); 4(5)-(*p*-methoxyphenylazo)-2-methylimidazole (Anulewicz & Maciejewska, 1996), $P2_1/c$, Z = 8 (Z' = 2), and a very interesting case of L-His-Gly hemihydrate (Steiner & Koellner, 1997), $P2_12_12_1$, Z = 8, Z' = 2, in which both symmetry-independent dipeptides are not only different tautomers but also their conformations are essentially different. There is also one example of a side-chain (hydroxylamine–aminonitrone) tautomerism: *N*-(4,5-dihydro-1*H*-imidazol-2-yl)-*N*-phenylhydroxylamine (Gdaniec *et al.*, 1995): $P2_1/c$, Z = 8 (Z' = 2).

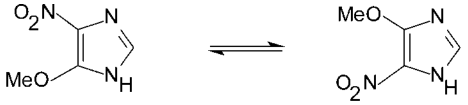
Two cases that belong to group (iii), *i.e.* in which the N—H proton is disordered, are similar in the sense that both are 4,5-symmetrically substituted and in both the disorder is a consequence of the special position of the molecule. In 2-amino-4,5-dicyanoimidazole (Hardgrove & Jons, 1991) two independent half-molecules lie perpendicular to the mirror plane in the space group $C2/m$, and in 4,5-diisopropylimidazole (Kuhn *et al.*, 2001) the molecule lies on a twofold axis in the space group $P4_32_12$. In principle, these cases should be also regarded as tautomerism, even though the tautomers are identical, still the proton exchange occurs between the ring N atoms.

In the course of wide studies on weak interactions in nitroimidazoles the crystal structure of a very simple derivative, 4-nitro-5-methoxyimidazole (1), was investigated. This compound offered the possibility of studying the interplay between strong and weak hydrogen bonds as opposed to the previously studied 1-phenyl-4-nitroimidazole, in which both medium- and high-resolution studies confirmed the decisive role of weak hydrogen bonds in crystal packing (Kubicki *et al.*, 2001, 2002). The ^{1}H NMR data suggested that there is only one tautomer present in solutions of (1).[1]

2. Experimental

The synthesis of the title compound was described elsewhere (Suwiński & Salwińska, 1987; Kulkarni *et al.*, 1987). Crystals appropriate for X-ray data collection were obtained by a slow evaporation from methanol solution at room temperature.

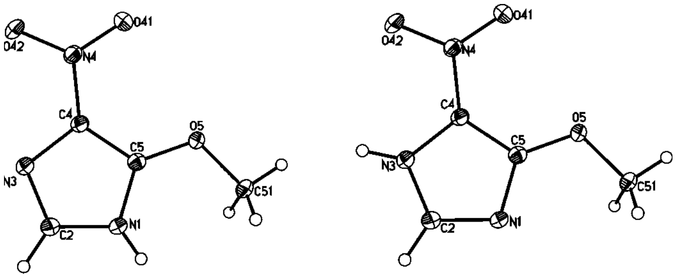
Crystal data, data collection and refinement parameters are summarized in Table 1. Diffraction data were collected with an Oxford Diffraction KUMA KM4CCD diffractometer at room temperature and 90 (1) K. The low temperature was controlled with an Oxford Instruments cryosystem cooling device. At both temperatures data collection was performed in six separate runs in order to cover the symmetry-independent area of reciprocal space (Oxford Diffraction, 2002*a*). There were 782 frames collected at both temperatures. Lorentz and polarization corrections were applied (Oxford Diffraction, 2002*b*) and then the data were corrected for absorption and merged with *SORTAV* (Blessing, 1989). Compound (1) crystallizes in a C-centered monoclinic unit cell with $Z = 8$. The systematic absences (hkl: $h + k = 2n + 1$, $h0l$: $l = 2n + 1$) allow for two space groups: centrosymmetric *C*2/*c* and non-centrosymmetric *Cc*. E-statistics strongly support the presence of a center of symmetry. The structure was solved and refined reasonably in both space groups (Table 1). In the *Cc* space group there are two symmetry-independent molecules in the asymmetric part of the unit cell ($Z' = 2$) and these molecules are different tautomers [see (I)]: 4-nitro-5-methoxyimidazole (1*A*) and 4-methoxy-5-nitroimidazole (1*B*). The difference-Fourier map calculated for the model without NH hydrogen atoms showed four almost equal peaks, two times higher than the next peak. When one physically reasonable pair of these peaks (*i.e.* avoiding short H···H contacts) was chosen, the remaining pair became invisible in the subsequent ΔF maps. (The two pairs of peaks would be related by symmetry in the group *C*2/*c*.) The positional and isotropic displacement parameters of the NH hydrogen atoms were successfully refined. The attempts to refine all four N—H hydrogen atoms that can be found in an initial map (with half occupancies) did not give an acceptable result. For *C*2/*c* the same physical situation is described with one molecule per asymmetric part of the unit cell ($Z' = 1$), but this molecule is disordered. There are two alternative positions for the H atom connected to the ring nitrogen, with site occupancy factor (s.o.f.) = 0.5 for each position (the exact value of the s.o.f. originates from the analysis of the hydrogen-bonding scheme). In this case the H atoms were also located in difference-Fourier maps and both positional and isotropic displacement parameters of all, including disordered, H atoms (*C*2/*c*) were refined.



1A 1B

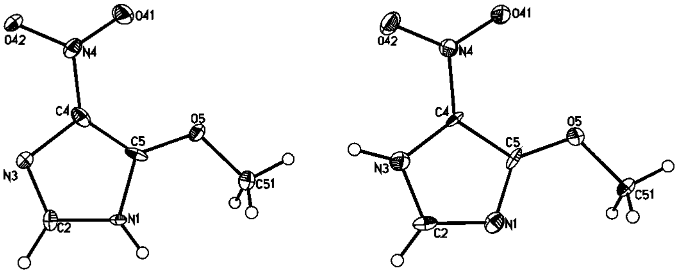
Apparently the non-centrosymmetric space group describes the physical reality more precisely, because at the basic level there are two different molecules in the crystal and therefore this case should be classified as possibility (ii). On the other hand, the deviations from the centrosymmetric arrangement are very small and mainly involve one H atom; the refinement procedure in a non-centrosymmetric space group therefore inevitably falls into the trap of huge correlations between refined parameters that lead to strange anisotropic displacement ellipsoids. The geometrical parameters obtained in this refinement should be regarded with utmost caution even though the s.u.'s are quite small.

There was no evidence of a phase transition or extraordinary structural changes between 295 and 90 K. The changes of unit-cell parameters with temperature are not uniform: parameters *b* and *c* decreased by a few percent (3.1 and 1.4%, respectively) while the *a* parameter remained stable and even increased a little (0.5%). Unit-cell volume, as expected, shrank by 3.8%.



(*a*) (*b*)

Figure 1
Displacement ellipsoid representation of both tautomers in the space group *C*2/*c* (Siemens, 1989): (*a*) 4-nitro-5-methoxyimidazole and (*b*) 4-methoxy-5-nitroimidazole. The ellipsoids are drawn at the 50% probability level; H atoms are depicted as spheres with arbitrary radii.



(*a*) (*b*)

Figure 2
Displacement ellipsoid representation of both tautomers in the space group *Cc* (Siemens, 1989): (*a*) 4-nitro-5-methoxyimidazole and (*b*) 4-methoxy-5-nitroimidazole. The ellipsoids are drawn at the 50% probability level; H atoms are depicted as spheres with arbitrary radii.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK5004). Services for accessing these data are described at the back of the journal.

Table 2
Selected geometric parameters (Å, °).

	Space group		
	*C*2/*c*	*Cc* mol. *A*	*Cc* mol. *B*
N1—C5	1.358 (1)	1.381 (2)	1.333 (2)
N1—C2	1.364 (1)	1.366 (2)	1.365 (2)
C2—N3	1.314 (1)	1.304 (2)	1.304 (2)
N3—C4	1.378 (1)	1.405 (2)	1.351 (2)
C4—C5	1.389 (1)	1.352 (2)	1.421 (2)
C4—N4	1.401 (1)	1.388 (2)	1.417 (2)
N4—O41	1.235 (1)	1.232 (1)	1.240 (1)
N4—O42	1.246 (1)	1.259 (1)	1.232 (1)
C5—O5	1.327 (1)	1.336 (2)	1.320 (2)
O5—C51	1.453 (1)	1.444 (2)	1.461 (2)
N1—H1	0.83 (2)	0.84 (1)	
N3—H3	0.87 (2)		0.90 (1)
C5—N1—C2	105.89 (8)	104.6 (1)	107.1 (1)
N3—C2—N1	112.77 (9)	113.4 (1)	112.0 (1)
C2—N3—C4	105.53 (8)	105.2 (1)	105.8 (1)
N3—C4—C5	108.56 (8)	108.4 (1)	108.8 (1)
N3—C4—N4	122.13 (8)	121.1 (1)	123.0 (1)
C5—C4—N4	129.31 (9)	130.5 (1)	128.3 (1)
O41—N4—O42	123.47 (8)	122.7 (1)	124.4 (1)
O41—N4—C4	118.36 (8)	118.2 (1)	118.5 (1)
O42—N4—C4	118.17 (8)	119.2 (1)	117.1 (1)
O5—C5—N1	125.74 (8)	124.4 (1)	126.8 (1)
O5—C5—C4	127.02 (8)	127.1 (1)	126.9 (1)
N1—C5—C4	107.25 (8)	108.5 (1)	106.3 (1)
C5—O5—C51	116.40 (7)	117.3 (1)	115.6 (1)
C5—N1—H1	129 (2)	129 (1)	
C2—N1—H1	125 (2)	127 (1)	
C2—N3—H3	125 (2)		127 (1)
C4—N3—H3	130 (2)		127 (1)

Regardless of the nature of the disorder, whether it is static or dynamic, the diffraction experiment (due to its time- and space-averaging nature) sees the structure as centrosymmetric. Therefore, the *C*2/*c* model, which in fact is the superposition of the two tautomeric structures, was chosen as the more appropriate, and the data for the *Cc* structure determination will be given only as a reference.

So, the crystal structure of (1) provides another case of centrosymmetric–noncentrosymmetric ambiguity (for example, Kubicki *et al.*, 2003, and references therein) that is, according to Marsh (1999), irresolvable in the absence of conclusive non-crystallographic evidence.

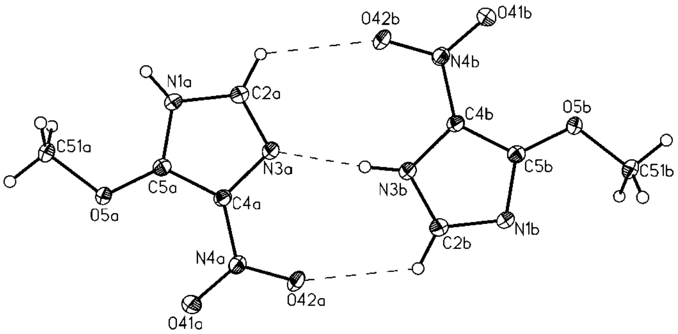

Figure 3
The hydrogen-bonded pair of tautomers (*C*2/*c* space group). Only one position of each N—H hydrogen atom is shown; hydrogen bonds are depicted as dashed lines. Displacement ellipsoids are drawn at the 50% probability level (Siemens, 1989).

Table 3
Hydrogen-bond data (*C*2/*c* model, Å, °).

D—H⋯*A*	*d*(*D*—H)	*d*(H⋯*A*)	*d*(*D*⋯*A*)	∠(*D*—H⋯*A*)
N1—H1⋯N1^{i}	0.83 (2)	2.04 (3)	2.8670 (16)	174 (2)
C2—H2⋯O42^{ii}	0.938 (12)	2.477 (12)	3.3749 (12)	160.4 (10)
C2—H2⋯O42^{iii}	0.938 (12)	2.509 (12)	3.1235 (13)	123.3 (9)
N3—H3⋯N3^{iii}	0.87 (2)	1.96 (2)	2.8307 (17)	176 (2)
C51—H51*A*⋯O41^{iv}	0.948 (13)	2.469 (13)	3.2918 (13)	145.2 (11)
C51—H51*A*⋯O5^{iv}	0.948 (13)	2.528 (13)	3.3283 (13)	142.3 (11)
C51—H51*C*⋯O42^{v}	0.995 (13)	2.660 (13)	3.6077 (14)	159.3 (11)

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

3. Results

3.1. Molecular structure

Fig. 1 shows the perspective views of the two tautomers as refined in the centrosymmetric space group; Fig. 2 shows these molecules from the results of the non-centrosymmetric block-diagonal refinement. The effects of correlations are clearly seen in the anisotropic ellipsoids. Only a very weak ISOR restraint for one atom was applied in this case, in order to visualize the range of uncontrolled effects in this refinement.

There should be differences in the geometries of the two tautomers, especially in their bond angles, because the protonation of the N atom results in the widening of the intraannular C—N—C angle. For 96 1*H*-imidazoles found in the CSD (Allen, 2002; only organic derivatives, with $R < 0.075$,

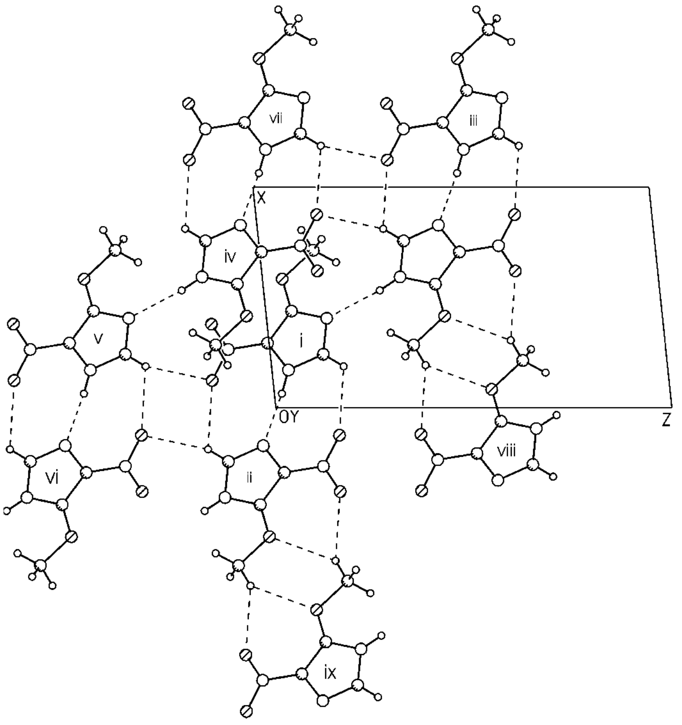

Figure 4
Hydrogen-bonding scheme as seen along the *y*-direction with the outline of the unit cell (Siemens, 1989). Hydrogen bonds are depicted as dashed lines. Symmetry codes: (i) $1-x, y, \frac{1}{2}-z$; (ii) $-1+x, 2-y, -\frac{1}{2}+z$; (iii) $2-x, 2-y, 1-z$; (iv) $x, 2-y, -\frac{1}{2}+z$; (v) $1-x, 2-y, -z$; (vi) $-1+x, 2-y, -z$; (vii) $2-x, y, \frac{1}{2}-x$; (viii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (ix) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

no fused rings, C2-unsubstituted) the mean value of C5—N1—C2 is 107.3 (9)° and the mean value of C2—N3—C4 is 105 (1)°. The differences should also be observed to some extent in the N—C bond lengths. For the same sample from the Cambridge Structural Database (CSD), the mean values of the C—N bond lengths are as follows: C1—N2 1.34 (1), C1—C5 1.37 (1), N3—C2 1.318 (8) and N3—C4 1.38 (2) Å.

In a centrosymmetric description these differences cancel each other out: the N atom that is protonated in one tautomer bears a lone pair in the other and *vice versa*. Not surprisingly, both intraannular C—N—C angles are almost equal, within the 3σ limit (Table 2). The N1—C5 and N1—C2 bond lengths are almost equal, but still there is a significant difference between the C2—N3 and N3—C4 bond lengths. It should be noted that there are no obvious abnormalities in the anisotropic displacement parameters refined in the centrosymmetric space group that could be caused by small differences in atomic positions. Deviations from the Hirshfeld's rigid-bond test (Hirshfeld, 1976) are largest in the methoxy group, but are small for the bonds in the ring.

The imidazole ring is almost ideally planar; the largest deviation from the least-squares plane is 0.0018 (6) Å. The substituents are also close to coplanarity: the dihedral angles between the imidazole ring plane and the planes of the nitro and methoxy groups are 1.3 (1) and 2.4 (1)°, respectively.

3.2. Crystal packing

The crystal packing is determined by a complicated system of hydrogen bonds, both strong and weak. Of course, in both space groups the packing schemes are identical, taking into account that a disorder in *C*2/*c* prevents impossibly short H···H contacts. This is another example of a situation mentioned by Gdaniec *et al.* (1995), in which the hydrogen-bond pattern proves not only the existence of both tautomers in the crystal, but also that they occur in equal amounts.

For the description of the hydrogen-bond scheme a graph-set notation will be used (Etter *et al.*, 1990; Bernstein *et al.*, 1995). Hydrogen-bond data are listed in Table 3.

The main hydrogen-bond motif is created by strong and linear intermolecular N—H···N bonds between different tautomers that make second-order $C_2^2(8)$ ~*ABAB*~ zigzag chains of molecules (second order because two different H atoms are involved in the motif), that expand infinitely along the [102] direction. Each *BA* pair of molecules is additionally connected by two relatively strong C2—H2···O42 hydrogen bonds that make second-order rings: non-centrosymmetric $R_2^2(8)$ and centrosymmetric $R_2^2(12)$ (Fig. 3). It might be noted that the proton transfer within the chain, accompanied by the rearrangement of bonds within the π-conjugated fragment [N1—C2═N3 and N1═C2—N3; *cf.* (1)] will interconvert the tautomers and change the direction of the chain.

The neighboring chains are connected by bifurcated C2—H2···O42 hydrogen bonds [$R_2^2(4)$ centrosymmetric rings]. As a result, a two-dimensional hydrogen-bonded layer is created (Fig. 4). The final element of the hydrogen-bond network is provided by bifurcated C51—H51*A*···O bonds that make a centrosymmetric dimeric $R_2^2(6)$ ring and a pair of $R_2^1(6)$ rings.

Two O atoms from the nitro group, O41 and O42, are involved in the hydrogen-bond system in a different way: the O42 atom participates in three hydrogen bonds, while O41 participates in only one. Interestingly, this difference is reflected in a small, but statistically significant, difference in N—O bond lengths: N4—O42 is more than 6σ longer than N4—O41.

4. Conclusions

The crystal structure of (1) has been successfully determined from single-crystal X-ray diffraction at 90 K. This is one of the very few (if not the only) case of a 4,5-unsymmetrically substituted imidazole derivative for which there are two annular tautomers in the crystal and they appear as one disordered molecule. The molecular structure is the superposition of these tautomeric forms. The hydrogen-bond pattern proves that there is an exact 50:50 mixture of both tautomers.

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