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# Crystal structure of (*E*)-2-[(4-hydroxybenzylidene)azaniumyl]benzoate

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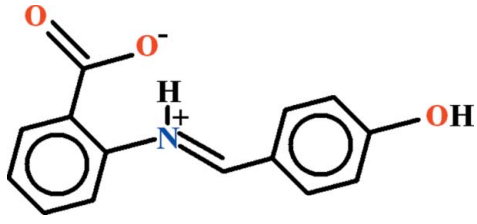
The title Schiff base, $C_{14}H_{11}NO_3$, crystallizes as a zwitterion (*i.e.* proton transfer from the carboxylic acid group to the imine N atom). The dihedral angle between the aromatic rings is 19.59 (6)° and an intramolecular N—H···O hydrogen bond closes an *S*(6) ring. In the crystal, inversion dimers linked by pairs of O—H···O hydrogen bonds generate $R_2^4(24)$ loops. The dimers are linked by C—H···O interactions, generating (211) sheets.

**Keywords:** crystal structure; Schiff bases; azanium–carboxylate zwitterion; hydrogen bonding.

**CCDC reference**: 1018737

## 1. Related literature

For related structures, see: Hang *et al.* (2010); Ligtenbarg *et al.* (1999); Trzesowska-Kruszynska (2010).




## 2. Experimental

### 2.1. Crystal data

$C_{14}H_{11}NO_3$
$M_r$ = 241.24
Monoclinic, $P2_1/n$
$a$ = 3.8612 (5) Å
$b$ = 15.280 (3) Å
$c$ = 18.604 (3) Å
$\beta$ = 90.347 (8)°
$V$ = 1097.6 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 296 K
0.38 × 0.17 × 0.15 mm

### 2.2. Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
$T_{min}$ = 0.962, $T_{max}$ = 0.985
17364 measured reflections
2089 independent reflections
1363 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.065

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.124
$S$ = 1.15
2089 reflections
169 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H3$A$···O1$^{i}$ | 0.95 (4) | 1.71 (4) | 2.656 (3) | 173 (3) |
| N1—H1···O1 | 1.00 (3) | 1.62 (3) | 2.522 (3) | 148 (2) |
| C6—H6···O2$^{ii}$ | 0.93 | 2.51 | 3.397 (4) | 160 |

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7268).

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# supporting information

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## Crystal structure of (*E*)-2-[(4-hydroxybenzylidene)azaniumyl]benzoate

**M. Nawaz Tahir, Abdul Haleem Khan and Hazoor Ahmad Shad**

### S1. Comment

The title compound (I), (Fig. 1) has been synthesized for forming different metal complexes.

The crystal structures of *N*-(2-Carboxyphenyl)salicylidenimine (Ligtenbarg *et al.*, 1999), 2-((4-(dimethylamino)benzylidene)ammonio) benzoate pentahydrate (Trzesowska-Kruszynska, 2010) and 2-[(2-hydroxy-4-methoxybenzylidene)azaniumyl]benzoate monohydrate (Hang, *et al.*, 2010) have been published which are related to the title compound (I).

The title compound has been crystalized in the zwitterion form. In (I) the moieties of 2-aminobenzoic acid A (C1—C7/N1/O1/O2) and the 4-hydroxybenzalehyde B (C8—C14/O3) are planar with r.m.s. deviation of 0.0133 and 0.0219 Å, respectively. The dihedral angle between A/B is 19.589 (58)°. In (I), *S*(6) ring motif is present due to H-bonding of N—H···O type (Table 1, Fig. 1). The molecules are dimerized from end to end due to H-bondings of O—H···O type (Table 1, Fig. 2) and form $R_2^4(24)$ loop. The dimers are further interlinked due to C—H···O bonds.

### S2. Experimental

Equimolar quantities of 2-aminobenzoic acid and 4-hydroxybenzaldehyde were refluxed in methanol along with few drops of acetic acid as catalyst for 2 h. The resulting solution was kept at room temperature which afforded yellow needles after two days.

### S3. Refinement

The coordinates of H1 and H3A were refined. The H-atoms were positioned geometrically (C–H = 0.93 Å) and refined as riding with $U_{iso}(H) = xU_{eq}(C, N, O)$, where $x = 1.5$ for hydroxy & $x = 1.2$ for other H-atoms.

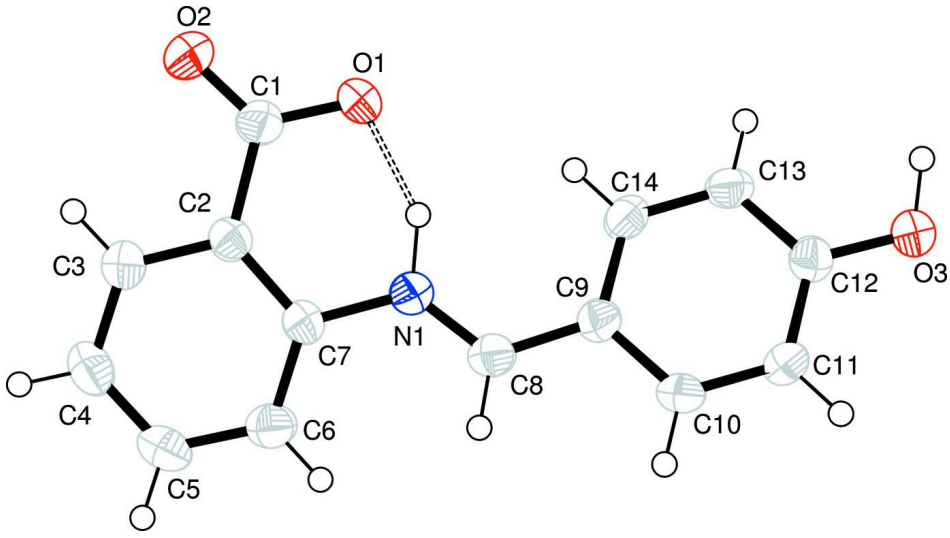


**Figure 1**

View of the title compound with displacement ellipsoids drawn at the 50% probability level. The dotted line represents the intramolecular H-bond.

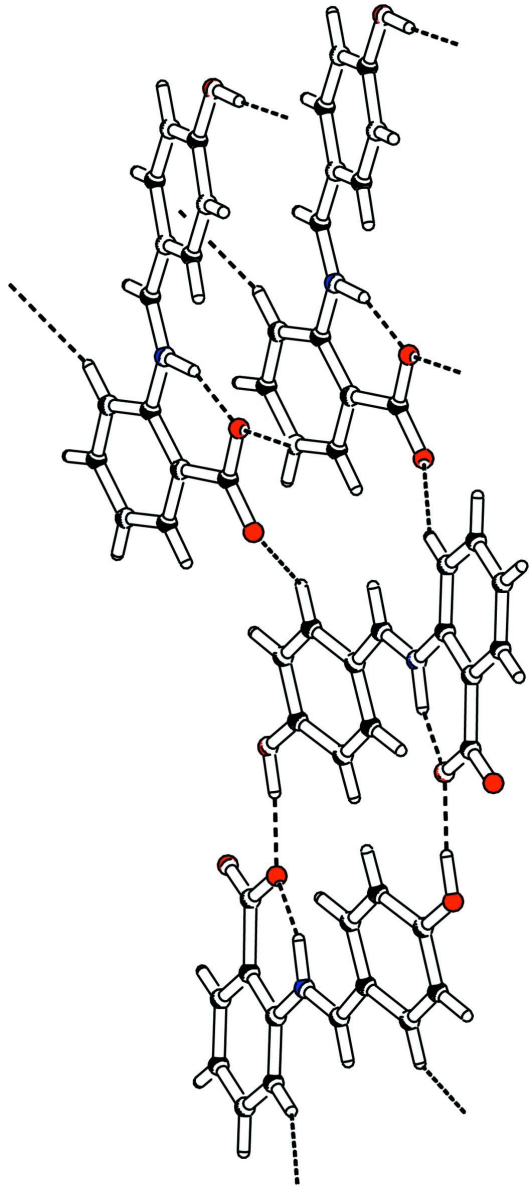

**Figure 2**

The partial packing, which shows that molecules form dimers which are interlinked.

### (*E*)-2-[(4-hydroxybenzylidene)azaniumyl]benzoate

*Crystal data*

$C_{14}H_{11}NO_3$
$M_r = 241.24$
Monoclinic, $P2_1/n$
$a = 3.8612$ (5) Å
$b = 15.280$ (3) Å
$c = 18.604$ (3) Å
$\beta = 90.347$ (8)°
$V = 1097.6$ (3) Å$^3$
$Z = 4$
$F(000) = 504$
$D_x = 1.460$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1363 reflections
$\theta = 1.8$–26.0°
$\mu = 0.10$ mm$^{-1}$
$T = 296$ K
Cut needle, yellow
0.38 × 0.17 × 0.15 mm

*Data collection*

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.00 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
$T_{min}$ = 0.962, $T_{max}$ = 0.985
17364 measured reflections
2089 independent reflections
1363 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.065
$\theta_{max}$ = 26.0°, $\theta_{min}$ = 1.7°
$h$ = −4→4
$k$ = −18→18
$l$ = −22→22

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.124
$S$ = 1.15
2089 reflections
169 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 1.0858P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger.

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.1341 (6) | −0.08844 (13) | 0.32981 (10) | 0.0469 (6) |
| O2 | 0.0144 (7) | −0.18735 (14) | 0.24574 (12) | 0.0580 (7) |
| O3 | 0.6380 (6) | 0.22716 (14) | 0.59807 (11) | 0.0489 (6) |
| H3A | 0.701 (9) | 0.177 (2) | 0.6251 (19) | 0.073* |
| N1 | −0.0068 (6) | 0.07058 (16) | 0.30803 (13) | 0.0360 (6) |
| H1 | 0.067 (7) | 0.016 (2) | 0.3337 (15) | 0.043* |
| C1 | 0.0114 (8) | −0.1120 (2) | 0.26817 (16) | 0.0394 (7) |
| C2 | −0.1414 (7) | −0.04003 (18) | 0.22116 (14) | 0.0328 (7) |
| C3 | −0.2813 (8) | −0.0637 (2) | 0.15519 (15) | 0.0398 (7) |
| H3 | −0.2817 | −0.1223 | 0.1417 | 0.048* |
| C4 | −0.4196 (8) | −0.0021 (2) | 0.10915 (16) | 0.0460 (8) |
| H4 | −0.5103 | −0.0192 | 0.0649 | 0.055* |
| C5 | −0.4233 (8) | 0.0847 (2) | 0.12868 (16) | 0.0461 (8) |
| H5 | −0.5171 | 0.1261 | 0.0975 | 0.055* |
| C6 | −0.2890 (8) | 0.1107 (2) | 0.19417 (16) | 0.0416 (8) |

| | | | | |
|---|---|---|---|---|
| H6 | −0.2931 | 0.1694 | 0.2074 | 0.050* |
| C7 | −0.1485 (7) | 0.04873 (18) | 0.23973 (14) | 0.0332 (7) |
| C8 | 0.0590 (7) | 0.14802 (19) | 0.33225 (15) | 0.0370 (7) |
| H8 | 0.0125 | 0.1955 | 0.3025 | 0.044* |
| C9 | 0.1993 (7) | 0.16514 (18) | 0.40216 (15) | 0.0342 (7) |
| C10 | 0.2987 (7) | 0.25053 (19) | 0.41916 (16) | 0.0384 (7) |
| H10 | 0.2674 | 0.2947 | 0.3854 | 0.046* |
| C11 | 0.4416 (8) | 0.27050 (19) | 0.48472 (16) | 0.0397 (7) |
| H11 | 0.5063 | 0.3278 | 0.4950 | 0.048* |
| C12 | 0.4901 (8) | 0.20511 (19) | 0.53595 (15) | 0.0365 (7) |
| C13 | 0.3814 (7) | 0.12005 (18) | 0.52047 (15) | 0.0375 (7) |
| H13 | 0.4051 | 0.0764 | 0.5550 | 0.045* |
| C14 | 0.2400 (8) | 0.10038 (19) | 0.45483 (15) | 0.0376 (7) |
| H14 | 0.1700 | 0.0433 | 0.4451 | 0.045* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0702 (15) | 0.0380 (12) | 0.0324 (12) | 0.0036 (11) | −0.0144 (11) | 0.0019 (9) |
| O2 | 0.0942 (19) | 0.0323 (12) | 0.0474 (14) | 0.0034 (13) | −0.0117 (13) | −0.0025 (11) |
| O3 | 0.0679 (16) | 0.0367 (13) | 0.0419 (13) | −0.0001 (11) | −0.0187 (11) | −0.0015 (10) |
| N1 | 0.0437 (15) | 0.0313 (14) | 0.0329 (13) | 0.0036 (11) | −0.0026 (11) | −0.0010 (11) |
| C1 | 0.0498 (19) | 0.0336 (17) | 0.0347 (17) | −0.0006 (14) | 0.0009 (15) | 0.0032 (14) |
| C2 | 0.0340 (16) | 0.0343 (16) | 0.0300 (15) | 0.0000 (13) | 0.0007 (13) | 0.0007 (12) |
| C3 | 0.0438 (18) | 0.0382 (18) | 0.0374 (17) | −0.0019 (14) | −0.0049 (14) | −0.0030 (14) |
| C4 | 0.0479 (19) | 0.056 (2) | 0.0344 (18) | 0.0010 (16) | −0.0085 (15) | −0.0005 (15) |
| C5 | 0.050 (2) | 0.048 (2) | 0.0400 (18) | 0.0060 (16) | −0.0051 (16) | 0.0115 (16) |
| C6 | 0.0443 (19) | 0.0354 (17) | 0.0452 (19) | 0.0038 (14) | −0.0015 (15) | 0.0032 (14) |
| C7 | 0.0370 (17) | 0.0347 (17) | 0.0278 (15) | −0.0001 (13) | −0.0005 (13) | 0.0003 (12) |
| C8 | 0.0401 (17) | 0.0319 (16) | 0.0390 (17) | 0.0000 (13) | −0.0009 (14) | 0.0033 (14) |
| C9 | 0.0350 (16) | 0.0313 (16) | 0.0362 (16) | 0.0019 (13) | −0.0024 (13) | −0.0017 (13) |
| C10 | 0.0439 (18) | 0.0305 (16) | 0.0407 (18) | 0.0027 (14) | −0.0066 (14) | 0.0064 (13) |
| C11 | 0.0461 (18) | 0.0271 (16) | 0.0457 (19) | −0.0011 (13) | −0.0075 (15) | −0.0018 (14) |
| C12 | 0.0389 (17) | 0.0359 (17) | 0.0345 (16) | 0.0020 (13) | −0.0027 (14) | −0.0028 (13) |
| C13 | 0.0472 (19) | 0.0289 (16) | 0.0365 (17) | 0.0018 (14) | 0.0006 (14) | 0.0047 (13) |
| C14 | 0.0442 (18) | 0.0280 (16) | 0.0404 (17) | −0.0022 (13) | 0.0000 (14) | −0.0035 (13) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.289 (3) | C5—H5 | 0.9300 |
| O2—C1 | 1.225 (3) | C6—C7 | 1.380 (4) |
| O3—C12 | 1.329 (3) | C6—H6 | 0.9300 |
| O3—H3A | 0.95 (4) | C8—C9 | 1.430 (4) |
| N1—C8 | 1.291 (3) | C8—H8 | 0.9300 |
| N1—C7 | 1.420 (3) | C9—C10 | 1.396 (4) |
| N1—H1 | 1.00 (3) | C9—C14 | 1.401 (4) |
| C1—C2 | 1.522 (4) | C10—C11 | 1.370 (4) |
| C2—C3 | 1.386 (4) | C10—H10 | 0.9300 |

| | | | |
|---|---|---|---|
| C2—C7 | 1.400 (4) | C11—C12 | 1.393 (4) |
| C3—C4 | 1.378 (4) | C11—H11 | 0.9300 |
| C3—H3 | 0.9300 | C12—C13 | 1.395 (4) |
| C4—C5 | 1.375 (4) | C13—C14 | 1.368 (4) |
| C4—H4 | 0.9300 | C13—H13 | 0.9300 |
| C5—C6 | 1.380 (4) | C14—H14 | 0.9300 |

| | | | |
|---|---|---|---|
| C12—O3—H3A | 111 (2) | C6—C7—N1 | 122.4 (3) |
| C8—N1—C7 | 127.0 (3) | C2—C7—N1 | 116.1 (2) |
| C8—N1—H1 | 122.7 (16) | N1—C8—C9 | 123.9 (3) |
| C7—N1—H1 | 109.9 (16) | N1—C8—H8 | 118.0 |
| O2—C1—O1 | 124.2 (3) | C9—C8—H8 | 118.0 |
| O2—C1—C2 | 119.2 (3) | C10—C9—C14 | 118.2 (3) |
| O1—C1—C2 | 116.6 (3) | C10—C9—C8 | 118.6 (3) |
| C3—C2—C7 | 117.6 (3) | C14—C9—C8 | 123.2 (3) |
| C3—C2—C1 | 117.9 (3) | C11—C10—C9 | 121.2 (3) |
| C7—C2—C1 | 124.5 (2) | C11—C10—H10 | 119.4 |
| C4—C3—C2 | 121.4 (3) | C9—C10—H10 | 119.4 |
| C4—C3—H3 | 119.3 | C10—C11—C12 | 120.1 (3) |
| C2—C3—H3 | 119.3 | C10—C11—H11 | 120.0 |
| C5—C4—C3 | 119.9 (3) | C12—C11—H11 | 120.0 |
| C5—C4—H4 | 120.0 | O3—C12—C11 | 117.9 (3) |
| C3—C4—H4 | 120.0 | O3—C12—C13 | 122.9 (3) |
| C4—C5—C6 | 120.5 (3) | C11—C12—C13 | 119.2 (3) |
| C4—C5—H5 | 119.8 | C14—C13—C12 | 120.5 (3) |
| C6—C5—H5 | 119.8 | C14—C13—H13 | 119.8 |
| C5—C6—C7 | 119.2 (3) | C12—C13—H13 | 119.8 |
| C5—C6—H6 | 120.4 | C13—C14—C9 | 120.8 (3) |
| C7—C6—H6 | 120.4 | C13—C14—H14 | 119.6 |
| C6—C7—C2 | 121.4 (3) | C9—C14—H14 | 119.6 |

| | | | |
|---|---|---|---|
| O2—C1—C2—C3 | 1.9 (4) | C8—N1—C7—C6 | −11.1 (5) |
| O1—C1—C2—C3 | −178.8 (3) | C8—N1—C7—C2 | 169.5 (3) |
| O2—C1—C2—C7 | −177.6 (3) | C7—N1—C8—C9 | 179.4 (3) |
| O1—C1—C2—C7 | 1.7 (4) | N1—C8—C9—C10 | 172.3 (3) |
| C7—C2—C3—C4 | 0.6 (4) | N1—C8—C9—C14 | −8.1 (5) |
| C1—C2—C3—C4 | −179.0 (3) | C14—C9—C10—C11 | 1.9 (4) |
| C2—C3—C4—C5 | −0.6 (5) | C8—C9—C10—C11 | −178.6 (3) |
| C3—C4—C5—C6 | 0.1 (5) | C9—C10—C11—C12 | 0.0 (5) |
| C4—C5—C6—C7 | 0.4 (5) | C10—C11—C12—O3 | 178.3 (3) |
| C5—C6—C7—C2 | −0.4 (4) | C10—C11—C12—C13 | −2.1 (4) |
| C5—C6—C7—N1 | −179.7 (3) | O3—C12—C13—C14 | −178.0 (3) |
| C3—C2—C7—C6 | 0.0 (4) | C11—C12—C13—C14 | 2.3 (4) |
| C1—C2—C7—C6 | 179.5 (3) | C12—C13—C14—C9 | −0.5 (4) |
| C3—C2—C7—N1 | 179.3 (3) | C10—C9—C14—C13 | −1.6 (4) |
| C1—C2—C7—N1 | −1.2 (4) | C8—C9—C14—C13 | 178.8 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3*A*···O1$^{i}$ | 0.95 (4) | 1.71 (4) | 2.656 (3) | 173 (3) |
| N1—H1···O1 | 1.00 (3) | 1.62 (3) | 2.522 (3) | 148 (2) |
| C6—H6···O2$^{ii}$ | 0.93 | 2.51 | 3.397 (4) | 160 |

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) −*x*−1/2, *y*+1/2, −*z*+1/2.