Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# *N*-(2-Aminophenyl)maleamic acid

**Norma Francenia Santos-Sánchez,[a] Raúl Salas-Coronado,[a] Adrián Peña-Hueso[b] and Angelina Flores-Parra[b]***

[a]Instituto de Agroindustrias, Universidad Tecnológica de la Mixteca, 69000 Huajuapan de León, Oaxaca, Mexico, and [b]Department of Chemistry, CINVESTAV-IPN, AP 14-740, 07000 México DF, Mexico
Correspondence e-mail: nsantos@mixteco.utm.mx

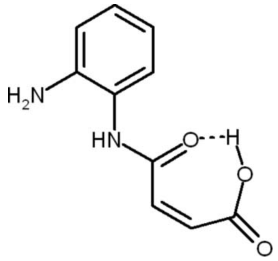
Received 10 August 2007; accepted 19 September 2007

Key indicators: single-crystal X-ray study; $T$ = 294 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.041; $wR$ factor = 0.051; data-to-parameter ratio = 8.1.

The title compound [also called ($Z$)-3-(2-aminophenylcarbamoyl)propenoic acid], $C_{10}H_{10}N_2O_3$, is a non-planar amidated maleic acid derivative, with the mean planes through the 2-aminophenyl and maleamic acid groups inclined at an angle of 43.08 (10)°. Symmetry-related molecules are linked by intermolecular N—H···N hydrogen bonds, forming centrosymmetric amine–amide dimers. The dimers are linked by N—H···O and C—H···O hydrogen bonds and weak N—H···$\pi$ and $\pi$–$\pi$ interactions [C-to-centroid distance 3.510 (3) Å] into a three-dimensional network.

## Related literature

For related literature, see: Bernstein *et al.* (1995); Vaupel *et al.* (2006).



## Experimental

### *Crystal data*

$C_{10}H_{10}N_2O_3$
$M_r$ = 206.2
Monoclinic, $P2_1/c$
$a$ = 7.3899 (2) Å
$b$ = 12.2135 (3) Å
$c$ = 12.2633 (3) Å
$\beta$ = 119.726 (1)°
$V$ = 961.19 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.11 mm$^{-1}$
$T$ = 294 K
0.25 × 0.25 × 0.1 mm

### *Data collection*

Nonius KappaCCD area-detector diffractometer
Absorption correction: none
4773 measured reflections
2418 independent reflections
1155 reflections with $I > 2.5\sigma(I)$
$R_{\rm int}$ = 0.039

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.051
$S$ = 1.01
1155 reflections
142 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.17 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···O4 | 0.87 | 1.62 | 2.492 (2) | 174 |
| N4—H4···N6$^{\rm i}$ | 0.87 | 2.17 | 3.009 (3) | 163 |
| N6—H61···O2$^{\rm ii}$ | 0.878 (19) | 2.125 (19) | 2.969 (3) | 161.0 (19) |
| C7—H7···O4$^{\rm iii}$ | 0.95 | 2.41 | 3.349 (3) | 166 |
| N6—H62···C9$^{\rm iii}$ | 0.85 (2) | 2.77 (2) | 3.496 (3) | 144.0 (17) |

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

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *PLATON* (Spek, 2003).

The authors acknowledge Sonia Araceli Sánchez Ruiz, Department of Chemistry, CINVESTAV-IPN, for the acquisition of the MS, IR, $^1$H and $^{13}$C NMR spectra.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2058).

## References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Vaupel, S., Brutschy, B., Tarakeshwar, P. & Kim, K. S. (2006). *J. Am. Chem. Soc.* **128**, 5416–5426.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

doi:10.1107/S1600536807046132

# supplementary materials

*Acta Cryst.* (2007). E**63**, o4156 [ **doi:10.1107/S1600536807046132** ]

# *N*-(2-Aminophenyl)maleamic acid

**N. F. Santos-Sánchez, R. Salas-Coronado, A. Peña-Hueso and A. Flores-Parra**

## Comment

The title compound, (**I**), has been prepared by condensation from maleic anhydride and *o*-phenylenediamine as a intermediary for the synthesis of 1,2,3,4-tetrahydroquinoxalin-2-ones.

In the molecular structure of compound (**I**), the C2—C3 bond length of the maleamic moiety proves to have a clear double bond character and the bonds C1—C2 and C3—C4 are clearly single bonds, which confirms localized bonding, Table 1. The maleamic moiety is characterized by a rather short and almost linear O—H···O intramolecular hydrogen bond forming an *S*(7) ring (Bernstein *et al.*, 1995), Figure 1. The C—O distances in the carboxylic acid group are consistent with the position of the carboxyl H atom deduced from difference maps. The title compound is non-planar with the mean planes through the 2-aminophenyl and maleamic acid groups being inclined against each other at an angle of 43.08 (10)°.

The crystal packing for (**I**) shows that the molecules are linked by two close to linear N—H···N hydrogen bonds (see Table 2 for geometric parameters and symmetry codes) to form centrosymmetric $R^2_2(10)$ dimers (Figure 2). These hydrogen bonds probably are the reason for the non-planarity of compound (**I**).

Adjacent dimers of (**I**) are linked by N—H···O and C—H···O hydrogen bonds and also by weaker N—H···π contacts and π···π stacking interactions. Amino atom N6 acts as a hydrogen-bond donor, *via* H61, to atom O2 in the molecule at (-*x*, *y* − 1/2, −*z* + 1/2), while atom C7 at (-*x*, *y* − 1/2, −*z* + 1/2), in turn, acts as donor to O2 at (*x*, *y* − 1, *z*). In this manner, a *C*(10) chain is formed (motif a, Figure 3.), running along the *c* axis. The arrangement of N6—H61···O2$^{ii}$, N6$^{ii}$—H61$^{ii}$···O2$^{iv}$, C7$^{iii}$—H7$^{iii}$···O4$^{iv}$, C7—H7···O4$^{iii}$ interactions can be described by the graph-set notation $R^4_4(28)$. Aromatic carbon atom C7 acts as a hydrogen-bond donor, *via* H7, to O4 in the molecule at (-*x* + 1, *y* - 1/2, -*z* + 3/2), while C7 at (−*x* + 1, *y* - 1/2, −*z* + 3/2), in turn, acts as a donor to O4 at (*x*, *y* − 1, *z*). In this manner, a *C*(7) zigzag chain (motif b) is formed, running along the *b* axis, Figure 3. The geometry of the hydrogen bonding is given in Table 2. The amine hydrogen atom H62 is forming a N—H···π interaction with aromatic carbon C9 at (−*x* + 1, *y* − 1/2, -*z* + 3/2). These interactions are dominated by dispersion energies, Vaupel *et al.* (2006). Lastly, maleamic moieties do interact with the C5—C10 benzene ring (centroid *Cg*) at (*x* - 1, −*y* + 3/2, *z* − 1/2), the distance C1···*Cg* is 3.510 (3) Å and the gamma angle is 22.8°, Figure 4.

## Experimental

To a solution of *o*-phenylenediamine (9.2 mmol) in THF (20 ml) is added a solution of maleic anhydride (0.91 g, 9.3 mmol) in THF (20 ml). The suspension was stirred for 12 h at room temperature. The mixture was filtered and the solvent distilled off. The residue was precipitated with a mixture of acetone/hexane to give a yellow solid (1.87 g, 98%), which was washed with ethyl ether and recrystallized from THF to give yellow crystals suitable for single-crystal X-ray diffraction (m.p. 412–413 K). $R_f$ (4:6:0.1, hexane: AcOEt: formic acid) 0.23. $^1$H NMR (300.13 MHz, DMSO-$d_6$): δ 9.85 (s, 1H, $CO_2H$), 8.04 (bs, 2H, $NH_2$), 7.14 (bd, *J* = 7.9 Hz, 1H, H10), 6.97 (td, *J* = 7.9, 1.2 Hz, 1H, H8), 6.74 (bd, *J* = 7.9 Hz, 1H, H7), 6.61 (d, *J* = 12.2

Hz, 1H, H3), 6.56 (td, *J* = 7.9, 1.0 Hz, 1H, H9), 6.27 (d, *J* = 12.2 Hz, 1H, H2); $^{13}$C NMR (75.47 MHz, DMSO-$d_6$): δ 167.5 ($CO_2$), 165.0 (C4), 143.9 (C5), 134.5 (C3), 130.6 (C2), 127.8 (C8), 127.0 (C10), 122.4 (C6), 116.8 (C9), 116.5 (C7). MS [EI, m/*z* (%)]: 206 (100), 160 (64), 147 (99), 119 (36). HRMS calcd for $[C_{10}H_{10}N_2O_3 + H]^+$ 207.0764, found 207.0769. F T–IR (KBr) (cm$^{-1}$): 3388, 3308, 1706, 1308, 839.

### Refinement

All non-hydrogen atoms were refined anisotropically, C—H and amide hydrogen were placed in calculated positions, with distances C—H = 0.95 Å, N—H = 0.87 Å and O—H = 0.87 Å and $U_{iso}$(H) = 1.2 $U_{eq}$ (C, N) or 1.5 $U_{eq}$ (O). The H atoms of the amine group were refined but the N—H distances were restrained to 0.87 (2) Å [$U_{iso}$(H) = 1.2 $U_{eq}$(N)].

### Figures

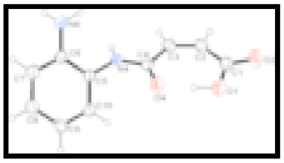


Fig. 1. A view of (**I**), showing 30% probability displacement ellipsoids (H atoms are draw as small spheres of arbitrary radii).

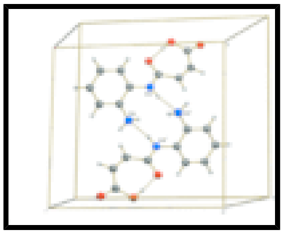


Fig. 2. Part of the crystal structure of (**I**), showing the formation of a hydrogen-bonded $R^2_2(10)$ dimer. Dashed lines indicate hydrogen bonds. Atoms marked with (i) are the at the symmetry related position (−*x* + 1, −*y* + 1, −*z* + 1).

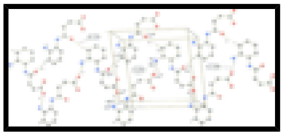


Fig. 3. The packing of (**I**), showing the $R^4_4(28)$ ring pattern. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. [Symmetry codes: (ii) -*x*, *y* − 1/2, −*z* + 1/2; (iii) −*x* + 1, *y* - 1/2, -*z* + 3/2; (iv) *x*, *y* − 1, *z*.]

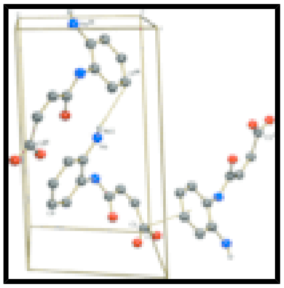


Fig. 4. Part of the crystal structure of (**I**), showing the formation weak N—H···π and π···π interactions. For clarity, all H atoms not involved in the motifs shown have been omitted [Symmetry codes: (iii) −*x* + 1, *y* − 1/2, −*z* + 3/2; (v) −1 + *x*, 3/2 − *y*, −1/2 + *z*.]

### (*Z*)-3-(2-aminophenylcarbamoyl)propenoic acid

*Crystal data*

| | |
|---|---|
| $C_{10}H_{10}N_2O_3$ | $F_{000}$ = 432 |
| $M_r$ = 206.2 | $D_x$ = 1.425 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo *K*α radiation<br>λ = 0.71073 Å |

Hall symbol: -P 2ybc
$a$ = 7.3899 (2) Å
$b$ = 12.2135 (3) Å
$c$ = 12.2633 (3) Å
$\beta$ = 119.7260 (10)°
$V$ = 961.19 (4) Å$^3$
$Z$ = 4

Cell parameters from 2535 reflections
$\theta$ = 1–29°
$\mu$ = 0.11 mm$^{-1}$
$T$ = 294 K
Prism, colourless
0.25 × 0.25 × 0.1 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
Monochromator: graphite
Detector resolution: 9 pixels mm$^{-1}$
$T$ = 291 K
$\varphi$ and $\omega$ scans
Absorption correction: none
4773 measured reflections
2418 independent reflections

1155 reflections with $I > 2.5\sigma(I)$
$R_{\rm int}$ = 0.039
$\theta_{\rm max}$ = 28.6°
$\theta_{\rm min}$ = 2.5°
$h = -9 \rightarrow 9$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 16$

*Refinement*

Refinement on $F$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.051
$S$ = 1.01
1155 reflections
142 parameters
2 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
Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.04P)^2]$,
where $P = (\max(F_o^2,0) + 2F_c^2)/3$ (Sheldrick, 1997)
$(\Delta/\sigma)_{\rm max}$ = 0.0002
$\Delta\rho_{\rm max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.17 e Å$^{-3}$
Extinction correction: none

*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$^2$ > 2sigma(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 ($Å^2$)*

| | *x* | *y* | *z* | $U_{\text{iso}}$*/$U_{\text{eq}}$ |
|---|---|---|---|---|
| C1 | 0.0694 (3) | 0.9421 (2) | 0.2238 (2) | 0.0631 |
| C2 | 0.1320 (3) | 0.82792 (19) | 0.21902 (19) | 0.0626 |
| C3 | 0.2464 (3) | 0.75461 (18) | 0.30799 (19) | 0.0566 |
| C4 | 0.3461 (3) | 0.76698 (16) | 0.44500 (18) | 0.0479 |
| C5 | 0.5634 (3) | 0.67199 (14) | 0.64461 (16) | 0.0421 |
| C6 | 0.5469 (3) | 0.57449 (15) | 0.69851 (16) | 0.0449 |
| C7 | 0.6578 (3) | 0.56406 (18) | 0.82783 (18) | 0.057 |
| C8 | 0.7808 (3) | 0.64865 (18) | 0.9029 (2) | 0.0633 |
| C9 | 0.7967 (3) | 0.74467 (17) | 0.84874 (19) | 0.0575 |
| C10 | 0.6885 (3) | 0.75622 (15) | 0.71998 (18) | 0.0491 |
| H1 | 0.2094 | 0.9452 | 0.392 | 0.1064* |
| H2 | 0.0782 | 0.8031 | 0.1371 | 0.0719* |
| H3 | 0.2663 | 0.6861 | 0.2818 | 0.0655* |
| H4 | 0.4646 | 0.6245 | 0.4705 | 0.0569* |
| H7 | 0.6456 | 0.4975 | 0.8645 | 0.0697* |
| H8 | 0.8545 | 0.6406 | 0.9915 | 0.0728* |
| H9 | 0.8829 | 0.8021 | 0.9008 | 0.0643* |
| H10 | 0.7023 | 0.8206 | 0.6838 | 0.0573* |
| H61 | 0.316 (3) | 0.5050 (17) | 0.5507 (16) | 0.0671* |
| H62 | 0.409 (3) | 0.4385 (16) | 0.6653 (18) | 0.0687* |
| N4 | 0.4533 (2) | 0.67995 (12) | 0.51109 (13) | 0.0474 |
| N6 | 0.4266 (3) | 0.48726 (14) | 0.62196 (17) | 0.0557 |
| O1 | 0.1358 (2) | 0.99089 (13) | 0.33127 (15) | 0.0797 |
| O2 | −0.0414 (3) | 0.99077 (16) | 0.12712 (16) | 0.0937 |
| O4 | 0.3304 (2) | 0.85106 (12) | 0.49678 (12) | 0.0711 |

*Atomic displacement parameters ($Å^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0556 (12) | 0.0661 (15) | 0.0542 (14) | −0.0072 (11) | 0.0170 (11) | 0.0160 (12) |
| C2 | 0.0636 (12) | 0.0744 (16) | 0.0390 (12) | −0.0143 (12) | 0.0172 (10) | −0.0011 (11) |
| C3 | 0.0666 (13) | 0.0534 (13) | 0.0449 (12) | −0.0047 (11) | 0.0240 (11) | −0.0063 (10) |
| C4 | 0.0549 (11) | 0.0432 (11) | 0.0430 (11) | −0.0034 (9) | 0.0222 (9) | −0.0036 (9) |
| C5 | 0.0471 (10) | 0.0398 (10) | 0.0399 (10) | 0.0036 (8) | 0.0218 (9) | −0.0006 (8) |
| C6 | 0.0513 (10) | 0.0395 (10) | 0.0478 (11) | 0.0024 (9) | 0.0276 (9) | −0.0007 (8) |
| C7 | 0.0703 (13) | 0.0511 (12) | 0.0524 (12) | 0.0047 (11) | 0.0327 (11) | 0.0069 (10) |
| C8 | 0.0742 (14) | 0.0642 (15) | 0.0421 (11) | 0.0112 (12) | 0.0217 (10) | 0.0035 (11) |
| C9 | 0.0591 (12) | 0.0517 (13) | 0.0479 (13) | 0.0028 (10) | 0.0160 (10) | −0.0073 (10) |
| C10 | 0.0542 (11) | 0.0399 (11) | 0.0499 (12) | −0.0002 (9) | 0.0233 (10) | −0.0017 (9) |
| N4 | 0.0635 (10) | 0.0367 (9) | 0.0416 (9) | 0.0011 (8) | 0.0257 (8) | −0.0037 (7) |
| N6 | 0.0686 (11) | 0.0415 (10) | 0.0590 (12) | −0.0063 (9) | 0.0331 (10) | −0.0004 (8) |
| O1 | 0.0946 (12) | 0.0566 (10) | 0.0640 (11) | 0.0115 (8) | 0.0210 (9) | 0.0103 (8) |
| O2 | 0.0916 (12) | 0.0978 (14) | 0.0665 (11) | 0.0065 (10) | 0.0199 (10) | 0.0353 (10) |
| O4 | 0.0936 (11) | 0.0542 (9) | 0.0460 (9) | 0.0215 (8) | 0.0197 (8) | −0.0042 (7) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.479 (3) | C6—N6 | 1.407 (2) |
| C1—O1 | 1.301 (3) | C7—C8 | 1.383 (3) |
| C1—O2 | 1.211 (2) | C7—H7 | 0.954 |
| C2—C3 | 1.339 (3) | C8—C9 | 1.381 (3) |
| C2—H2 | 0.929 | C8—H8 | 0.948 |
| C3—C4 | 1.470 (3) | C9—C10 | 1.379 (3) |
| C3—H3 | 0.933 | C9—H9 | 0.949 |
| C4—N4 | 1.333 (2) | C10—H10 | 0.932 |
| C4—O4 | 1.243 (2) | H1—O1 | 0.872 |
| C5—C6 | 1.396 (3) | H4—N4 | 0.869 |
| C5—C10 | 1.386 (2) | H61—N6 | 0.879 (15) |
| C5—N4 | 1.425 (2) | H62—N6 | 0.849 (15) |
| C6—C7 | 1.383 (3) | | |
| C2—C1—O1 | 120.3 (2) | C6—C7—H7 | 118.5 |
| C2—C1—O2 | 119.8 (2) | C8—C7—H7 | 120.5 |
| O1—C1—O2 | 119.9 (2) | C7—C8—C9 | 119.90 (19) |
| C1—C2—C3 | 133.0 (2) | C7—C8—H8 | 120 |
| C1—C2—H2 | 112.1 | C9—C8—H8 | 120.1 |
| C3—C2—H2 | 115 | C8—C9—C10 | 119.90 (19) |
| C2—C3—C4 | 128.2 (2) | C8—C9—H9 | 119.5 |
| C2—C3—H3 | 117.6 | C10—C9—H9 | 120.6 |
| C4—C3—H3 | 114.2 | C5—C10—C9 | 120.29 (17) |
| C3—C4—N4 | 115.02 (17) | C5—C10—H10 | 120.1 |
| C3—C4—O4 | 123.22 (18) | C9—C10—H10 | 119.6 |
| N4—C4—O4 | 121.74 (17) | C5—N4—C4 | 125.55 (15) |
| C6—C5—C10 | 120.22 (17) | C5—N4—H4 | 116.3 |
| C6—C5—N4 | 117.91 (16) | C4—N4—H4 | 118 |
| C10—C5—N4 | 121.85 (16) | C6—N6—H61 | 116.5 (14) |
| C5—C6—C7 | 118.70 (17) | C6—N6—H62 | 110.8 (15) |
| C5—C6—N6 | 120.31 (17) | H61—N6—H62 | 116.1 (19) |
| C7—C6—N6 | 120.95 (18) | H1—O1—C1 | 109.5 |
| C6—C7—C8 | 120.98 (19) | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···O4 | 0.87 | 1.62 | 2.492 (2) | 174 |
| N4—H4···N6$^{i}$ | 0.87 | 2.17 | 3.009 (3) | 163 |
| N6—H61···O2$^{ii}$ | 0.878 (19) | 2.125 (19) | 2.969 (3) | 161.0 (19) |
| C7—H7···O4$^{iii}$ | 0.95 | 2.41 | 3.349 (3) | 166 |
| N6—H62···C9$^{iii}$ | 0.85 (2) | 2.77 (2) | 3.496 (3) | 144.0 (17) |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, y-1/2, -z+1/2$; (iii) $-x+1, y-1/2, -z+3/2$.

**Fig. 1**

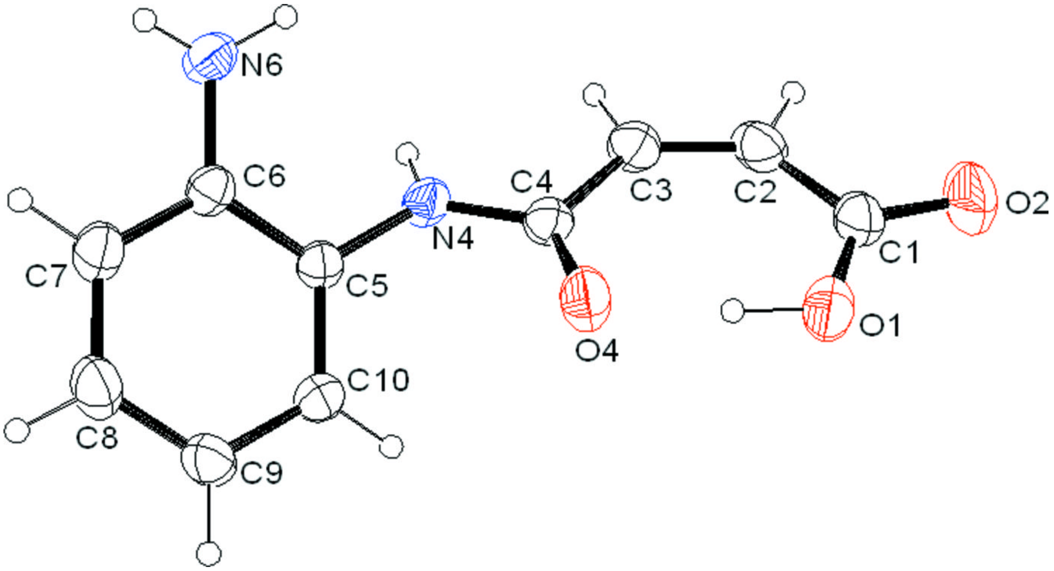


**Fig. 2**

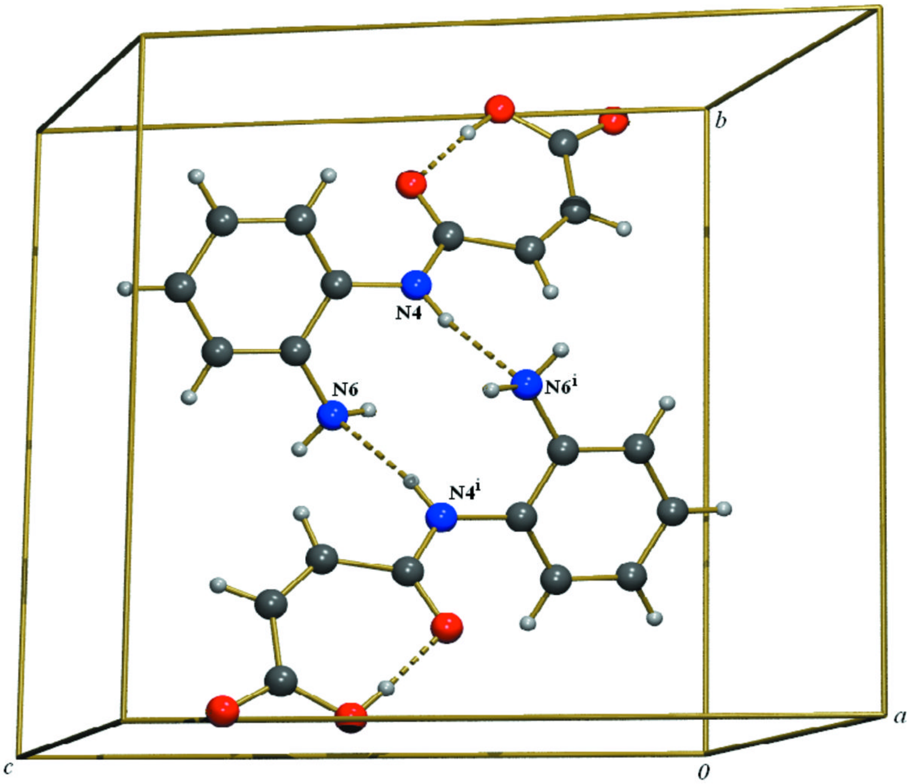


**Fig. 3**

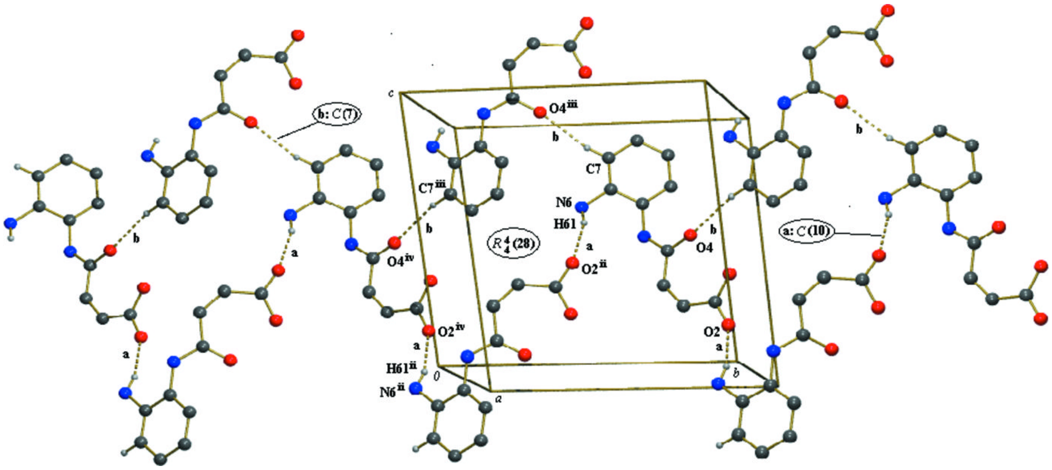

b: C(7)
O4iii
b
C7
c
C7iii
N6
H61
b
$R^4_4(28)$
a
O2ii
b
O4
a: C(10)
b
a
b
O4iv
a
O2iv
a
H61ii
N6ii
0
a
O2
a
b

**Fig. 4**