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Published

2010

Journal Title

Acta Crystallographica. Section E: Structure Reports Online

DOI

[10.1107/S160053681002581X](https://doi.org/10.1107/S160053681002581X)

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Guanidinium 3-nitrobenzoate

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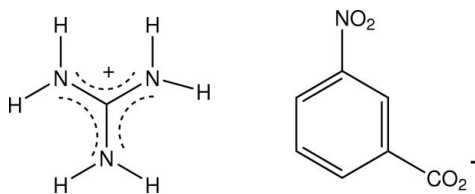
Received 25 May 2010; accepted 1 July 2010

Key indicators: single-crystal X-ray study; $T = 297$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.035; wR factor = 0.096; data-to-parameter ratio = 7.4.

The title compound, $\text{CH}_6\text{N}_3^+\cdot\text{C}_7\text{H}_4\text{NO}_4^-$, an anhydrous guanidinium salt, shows a $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bond network in which the guanidinium cation is involved in three cyclic $R_2^1(6)$ hydrogen-bonding associations with separate carboxylate O-atom acceptors. Further peripheral associations include a cyclic $R_1^2(4)$ cation-anion interaction, forming interlinked undulating sheets in the three-dimensional structure.

Related literature

For the structures of other guanidinium benzoate salts, see: Kleb *et al.* (1998); Pereira Silva *et al.* (2007, 2010). For graph-set analysis, see: Etter *et al.* (1990).



Experimental

Crystal data

$\text{CH}_6\text{N}_3^+\cdot\text{C}_7\text{H}_4\text{NO}_4^-$ $V = 1027.6$ (2) Å³
 $M_r = 226.20$ $Z = 4$
 Orthorhombic, $P2_12_12_1$ $\text{Mo } K\alpha$ radiation
 $a = 7.3978$ (12) Å $\mu = 0.12$ mm⁻¹
 $b = 10.1302$ (12) Å $T = 297$ K
 $c = 13.7118$ (17) Å $0.30 \times 0.30 \times 0.20$ mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer 7455 measured reflections
 Absorption correction: multi-scan 1252 independent reflections
 (*CrysAlis PRO*; Oxford Diffraction, 2009) 1092 reflections with $I > 2\sigma(I)$
 $T_{\min} = 0.94$, $T_{\max} = 0.98$ $R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$ H atoms treated by a mixture of independent and constrained refinement
 $wR(F^2) = 0.096$
 $S = 1.03$
 1252 reflections
 169 parameters
 $\Delta\rho_{\text{max}} = 0.15$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{N1G}-\text{H11G}\cdots\text{O12}$ | 0.82 (3) | 2.48 (3) | 3.161 (3) | 142 (3) |
| $\text{N1G}-\text{H12G}\cdots\text{O12}^i$ | 0.83 (3) | 2.09 (3) | 2.887 (3) | 162 (3) |
| $\text{N2G}-\text{H21G}\cdots\text{O11}^i$ | 0.91 (3) | 2.42 (3) | 3.292 (3) | 160 (2) |
| $\text{N2G}-\text{H21G}\cdots\text{O12}^i$ | 0.91 (3) | 2.43 (3) | 3.159 (3) | 137 (2) |
| $\text{N2G}-\text{H22G}\cdots\text{O11}^{ii}$ | 0.86 (3) | 2.29 (3) | 3.020 (3) | 143 (3) |
| $\text{N3G}-\text{H31G}\cdots\text{O11}^{ii}$ | 0.86 (3) | 1.97 (3) | 2.783 (3) | 157 (3) |
| $\text{N3G}-\text{H32G}\cdots\text{O12}$ | 0.91 (3) | 1.90 (3) | 2.794 (3) | 166 (3) |

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

The authors acknowledge financial support from the Australian Research Council, the Faculty of Science and Technology, Queensland University of Technology and the School of Biomolecular and Physical Sciences, Griffith University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BV2146).

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supplementary materials

Acta Cryst. (2010). E66, o1946 [doi:10.1107/S160053681002581X]

Guanidinium 3-nitrobenzoate

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Comment

The structures of the guanidinium salts of the simple benzoic acids are not numerous in the crystallographic literature, being limited to the benzoate (Pereira Silva *et al.*, 2007), 4-aminobenzoate (Pereira Silva *et al.*, 2010) and 4-nitrobenzoate (Kleb *et al.*, 1998). In these anhydrous structures and those of the anhydrous guanidinium salts of aromatic carboxylates generally, the cations give variously cyclic hydrogen-bonding interactions which may be classified by the graph sets $R^2_2(8)$, $R^2_1(4)$ or $R^1_2(6)$ (Etter *et al.*, 1990). Our 1:1 stoichiometric reaction of 3-nitrobenzoic acid with guanidinium carbonate in methanol gave large relatively hard, chemically stable crystals of guanidinium 3-nitrobenzoate, $\text{CH}_6\text{N}_3^+ \text{C}_7\text{H}_4\text{NO}_4^-$ (I), and the structure is reported here.

In the structure of (I) each guanidinium cation is involved in three cyclic $R^1_2(6)$ hydrogen-bonding associations (Table 1) with separate carboxylate O-acceptors (Figs. 1, 2). Further peripheral associations include a cyclic $R^2_1(4)$ cation–anion interaction, form inter-linked undulating sheets which give a three-dimensional framework structure (Fig. 3).

The carboxylate group of the anion is rotated slightly out of the plane of the benzene ring [torsion angle C2–C1–C11–O11, 160.0 (2)°]. However, the unassociated nitro group is essentially coplanar with the ring [torsion angle C2–C3–N31–O32, 174.4 (2)°].

Experimental

The title compound was synthesized by heating together under reflux for 10 minutes 1 mmol of 3-nitrobenzoic acid and 0.5 mmol of guanidine carbonate in 50 ml of methanol. After concentration to *ca* 30 ml, partial room temperature evaporation of the hot-filtered solution gave large colourless plates (m.p. 514 K) from which a suitable analytical specimen was cleaved.

Refinement

Guanidinium hydrogen atoms were located by difference methods and their positional and isotropic displacement parameters were refined. The H atoms of the aromatic ring of the anion were included in the refinement in calculated positions (C–H = 0.93 Å) and allowed to ride, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Friedel pairs were merged in the data set used for final structure refinement.

Figures

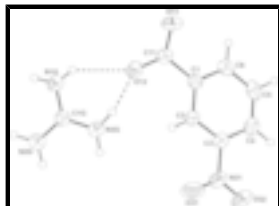


Fig. 1. The molecular configuration and atom-numbering scheme for the cation and anion species in (I). Non-H atoms are shown as 40% probability ellipsoids. Inter-ion hydrogen bonds are shown as dashed lines.

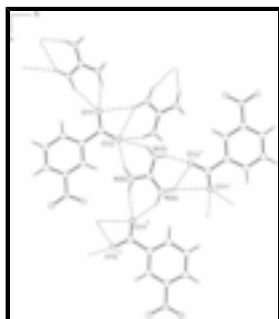


Fig. 2. Peripheral hydrogen-bonding extension of the $R_2^1(6)$ - associated guanidinium-tris(3-nitrobenzoate) structures of (I), viewed down the a cell direction. For symmetry codes, see Table 1. Hydrogen bonds are shown as dashed lines.

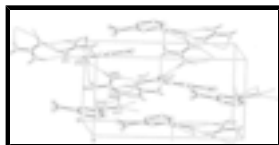
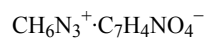


Fig. 3. The three-dimensional structure of (I) viewed down the approximate b cell direction. Non-associative H atoms are omitted.

Guanidinium 3-nitrobenzoate

Crystal data



$M_r = 226.20$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 7.3978$ (12) Å

$b = 10.1302$ (12) Å

$c = 13.7118$ (17) Å

$V = 1027.6$ (2) Å³

$Z = 4$

$F(000) = 472$

$D_x = 1.462$ Mg m⁻³

Melting point: 514 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2964 reflections

$\theta = 3.0$ – 28.9°

$\mu = 0.12$ mm⁻¹

$T = 297$ K

Block, colourless

$0.30 \times 0.30 \times 0.20$ mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Radiation source: Enhance (Mo) X-ray source graphite

ω scans

Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)

1252 independent reflections

1092 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\text{max}} = 26.5^\circ$, $\theta_{\text{min}} = 3.0^\circ$

$h = -9 \rightarrow 9$

$T_{\min} = 0.94$, $T_{\max} = 0.98$
7455 measured reflections

$k = -12 \rightarrow 11$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.096$

$S = 1.03$

1252 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

$w = 1/[\sigma^2(F_o^2) + (0.0716P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|--------------|---------------|----------------------------------|
| O11 | 0.8853 (3) | 0.39642 (19) | -0.15616 (11) | 0.0763 (7) |
| O12 | 0.8391 (3) | 0.51830 (14) | -0.02410 (12) | 0.0587 (5) |
| O31 | 0.9478 (4) | 0.2929 (2) | 0.29189 (13) | 0.0891 (8) |
| O32 | 0.8919 (4) | 0.0871 (2) | 0.30563 (13) | 0.0879 (8) |
| N31 | 0.9085 (3) | 0.1871 (2) | 0.25680 (14) | 0.0582 (6) |
| C1 | 0.8552 (3) | 0.28643 (18) | -0.00456 (13) | 0.0395 (5) |
| C2 | 0.8834 (3) | 0.29418 (19) | 0.09621 (14) | 0.0395 (5) |
| C3 | 0.8802 (3) | 0.1785 (2) | 0.15053 (15) | 0.0438 (6) |
| C4 | 0.8496 (3) | 0.0567 (2) | 0.10846 (18) | 0.0546 (7) |
| C5 | 0.8224 (3) | 0.0507 (2) | 0.00897 (18) | 0.0579 (8) |
| C6 | 0.8262 (3) | 0.1633 (2) | -0.04688 (16) | 0.0487 (6) |
| C11 | 0.8592 (3) | 0.4098 (2) | -0.06632 (14) | 0.0472 (6) |
| N1G | 0.5698 (4) | 0.7518 (2) | 0.02372 (14) | 0.0596 (7) |
| N2G | 0.5023 (3) | 0.7924 (2) | 0.18458 (16) | 0.0624 (7) |
| N3G | 0.6559 (3) | 0.6050 (2) | 0.14213 (17) | 0.0599 (7) |
| C1G | 0.5763 (3) | 0.7166 (2) | 0.11723 (14) | 0.0468 (6) |

supplementary materials

| | | | | |
|------|-----------|-----------|------------|------------|
| H2 | 0.90390 | 0.37520 | 0.12620 | 0.0470* |
| H4 | 0.84730 | -0.01950 | 0.14630 | 0.0660* |
| H5 | 0.80130 | -0.03050 | -0.02060 | 0.0690* |
| H6 | 0.80920 | 0.15720 | -0.11390 | 0.0580* |
| H11G | 0.617 (4) | 0.701 (3) | -0.015 (2) | 0.070 (9)* |
| H12G | 0.514 (4) | 0.821 (3) | 0.012 (2) | 0.072 (8)* |
| H21G | 0.444 (4) | 0.869 (3) | 0.170 (2) | 0.077 (9)* |
| H22G | 0.506 (4) | 0.767 (3) | 0.244 (2) | 0.065 (8)* |
| H31G | 0.666 (4) | 0.588 (3) | 0.203 (2) | 0.065 (8)* |
| H32G | 0.715 (4) | 0.563 (3) | 0.093 (2) | 0.073 (9)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O11 | 0.1174 (16) | 0.0759 (12) | 0.0357 (8) | 0.0071 (13) | 0.0050 (10) | 0.0078 (8) |
| O12 | 0.0866 (12) | 0.0375 (7) | 0.0520 (8) | -0.0007 (8) | 0.0034 (9) | 0.0074 (6) |
| O31 | 0.148 (2) | 0.0728 (12) | 0.0464 (9) | -0.0228 (14) | -0.0197 (12) | 0.0015 (9) |
| O32 | 0.1360 (19) | 0.0687 (11) | 0.0591 (11) | 0.0044 (13) | 0.0017 (12) | 0.0305 (9) |
| N31 | 0.0728 (11) | 0.0565 (11) | 0.0452 (10) | 0.0004 (11) | -0.0036 (9) | 0.0113 (8) |
| C1 | 0.0411 (9) | 0.0384 (10) | 0.0390 (9) | -0.0016 (9) | 0.0000 (9) | -0.0014 (8) |
| C2 | 0.0476 (10) | 0.0313 (8) | 0.0395 (9) | -0.0005 (9) | -0.0007 (8) | 0.0007 (7) |
| C3 | 0.0486 (10) | 0.0413 (10) | 0.0415 (10) | 0.0011 (9) | -0.0006 (9) | 0.0044 (8) |
| C4 | 0.0643 (13) | 0.0340 (10) | 0.0656 (13) | -0.0007 (10) | 0.0029 (12) | 0.0083 (10) |
| C5 | 0.0679 (15) | 0.0348 (10) | 0.0710 (15) | -0.0073 (10) | 0.0012 (13) | -0.0151 (10) |
| C6 | 0.0527 (11) | 0.0490 (11) | 0.0445 (10) | -0.0037 (10) | 0.0000 (9) | -0.0100 (9) |
| C11 | 0.0597 (12) | 0.0444 (10) | 0.0375 (10) | 0.0004 (10) | 0.0016 (10) | 0.0038 (9) |
| N1G | 0.0873 (16) | 0.0448 (10) | 0.0467 (12) | 0.0052 (11) | 0.0022 (11) | 0.0093 (9) |
| N2G | 0.0885 (15) | 0.0519 (11) | 0.0469 (11) | 0.0123 (12) | 0.0033 (11) | -0.0015 (9) |
| N3G | 0.0854 (14) | 0.0511 (11) | 0.0433 (10) | 0.0130 (12) | 0.0016 (11) | 0.0069 (9) |
| C1G | 0.0588 (12) | 0.0398 (10) | 0.0418 (11) | -0.0032 (10) | -0.0027 (9) | 0.0025 (9) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|-------------|-------------|----------|-----------|
| O11—C11 | 1.254 (2) | N3G—H32G | 0.91 (3) |
| O12—C11 | 1.251 (3) | C1—C6 | 1.392 (3) |
| O31—N31 | 1.210 (3) | C1—C11 | 1.510 (3) |
| O32—N31 | 1.221 (3) | C1—C2 | 1.400 (3) |
| N31—C3 | 1.475 (3) | C2—C3 | 1.389 (3) |
| N1G—C1G | 1.332 (3) | C3—C4 | 1.381 (3) |
| N2G—C1G | 1.320 (3) | C4—C5 | 1.380 (3) |
| N3G—C1G | 1.320 (3) | C5—C6 | 1.374 (3) |
| N1G—H12G | 0.83 (3) | C2—H2 | 0.9300 |
| N1G—H11G | 0.82 (3) | C4—H4 | 0.9300 |
| N2G—H22G | 0.86 (3) | C5—H5 | 0.9300 |
| N2G—H21G | 0.91 (3) | C6—H6 | 0.9300 |
| N3G—H31G | 0.86 (3) | | |
| O31—N31—O32 | 122.8 (2) | C2—C3—C4 | 122.2 (2) |
| O31—N31—C3 | 118.64 (19) | C3—C4—C5 | 118.4 (2) |

| | | | |
|---------------|-------------|---------------|-------------|
| O32—N31—C3 | 118.60 (19) | C4—C5—C6 | 120.8 (2) |
| C1G—N1G—H12G | 115.5 (19) | C1—C6—C5 | 121.0 (2) |
| H11G—N1G—H12G | 128 (3) | O11—C11—C1 | 117.67 (18) |
| C1G—N1G—H11G | 116 (2) | O12—C11—C1 | 117.73 (17) |
| H21G—N2G—H22G | 119 (3) | O11—C11—O12 | 124.6 (2) |
| C1G—N2G—H21G | 122.6 (18) | C3—C2—H2 | 121.00 |
| C1G—N2G—H22G | 119 (2) | C1—C2—H2 | 121.00 |
| H31G—N3G—H32G | 126 (3) | C3—C4—H4 | 121.00 |
| C1G—N3G—H32G | 115.1 (19) | C5—C4—H4 | 121.00 |
| C1G—N3G—H31G | 118 (2) | C4—C5—H5 | 120.00 |
| C6—C1—C11 | 120.72 (17) | C6—C5—H5 | 120.00 |
| C2—C1—C11 | 120.29 (17) | C5—C6—H6 | 120.00 |
| C2—C1—C6 | 118.99 (17) | C1—C6—H6 | 119.00 |
| C1—C2—C3 | 118.66 (18) | N2G—C1G—N3G | 120.2 (2) |
| N31—C3—C4 | 119.27 (19) | N1G—C1G—N2G | 120.2 (2) |
| N31—C3—C2 | 118.53 (18) | N1G—C1G—N3G | 119.6 (2) |
| O31—N31—C3—C2 | -5.8 (3) | C2—C1—C11—O12 | -18.9 (3) |
| O31—N31—C3—C4 | 174.9 (2) | C6—C1—C11—O11 | -19.1 (3) |
| O32—N31—C3—C2 | 174.4 (2) | C6—C1—C11—O12 | 162.0 (2) |
| O32—N31—C3—C4 | -4.9 (3) | C1—C2—C3—N31 | -179.5 (2) |
| C6—C1—C2—C3 | -0.4 (3) | C1—C2—C3—C4 | -0.2 (3) |
| C11—C1—C2—C3 | -179.5 (2) | N31—C3—C4—C5 | 179.6 (2) |
| C2—C1—C6—C5 | 1.0 (3) | C2—C3—C4—C5 | 0.4 (3) |
| C11—C1—C6—C5 | -180.0 (2) | C3—C4—C5—C6 | 0.2 (3) |
| C2—C1—C11—O11 | 160.0 (2) | C4—C5—C6—C1 | -0.8 (3) |

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1G—H11G \cdots O12 | 0.82 (3) | 2.48 (3) | 3.161 (3) | 142 (3) |
| N1G—H12G \cdots O12 ⁱ | 0.83 (3) | 2.09 (3) | 2.887 (3) | 162 (3) |
| N2G—H21G \cdots O11 ⁱ | 0.91 (3) | 2.42 (3) | 3.292 (3) | 160 (2) |
| N2G—H21G \cdots O12 ⁱ | 0.91 (3) | 2.43 (3) | 3.159 (3) | 137 (2) |
| N2G—H22G \cdots O11 ⁱⁱ | 0.86 (3) | 2.29 (3) | 3.020 (3) | 143 (3) |
| N3G—H31G \cdots O11 ⁱⁱ | 0.86 (3) | 1.97 (3) | 2.783 (3) | 157 (3) |
| N3G—H32G \cdots O12 | 0.91 (3) | 1.90 (3) | 2.794 (3) | 166 (3) |
| C4—H4 \cdots O31 ⁱⁱⁱ | 0.93 | 2.57 | 3.355 (3) | 142 |

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

Fig. 1

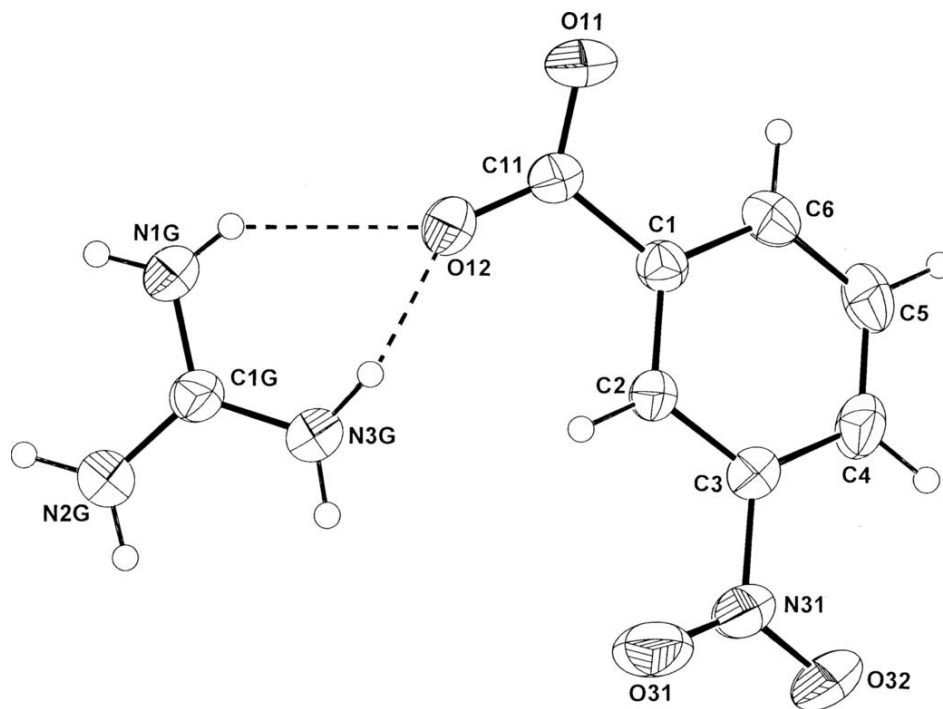


Fig. 2

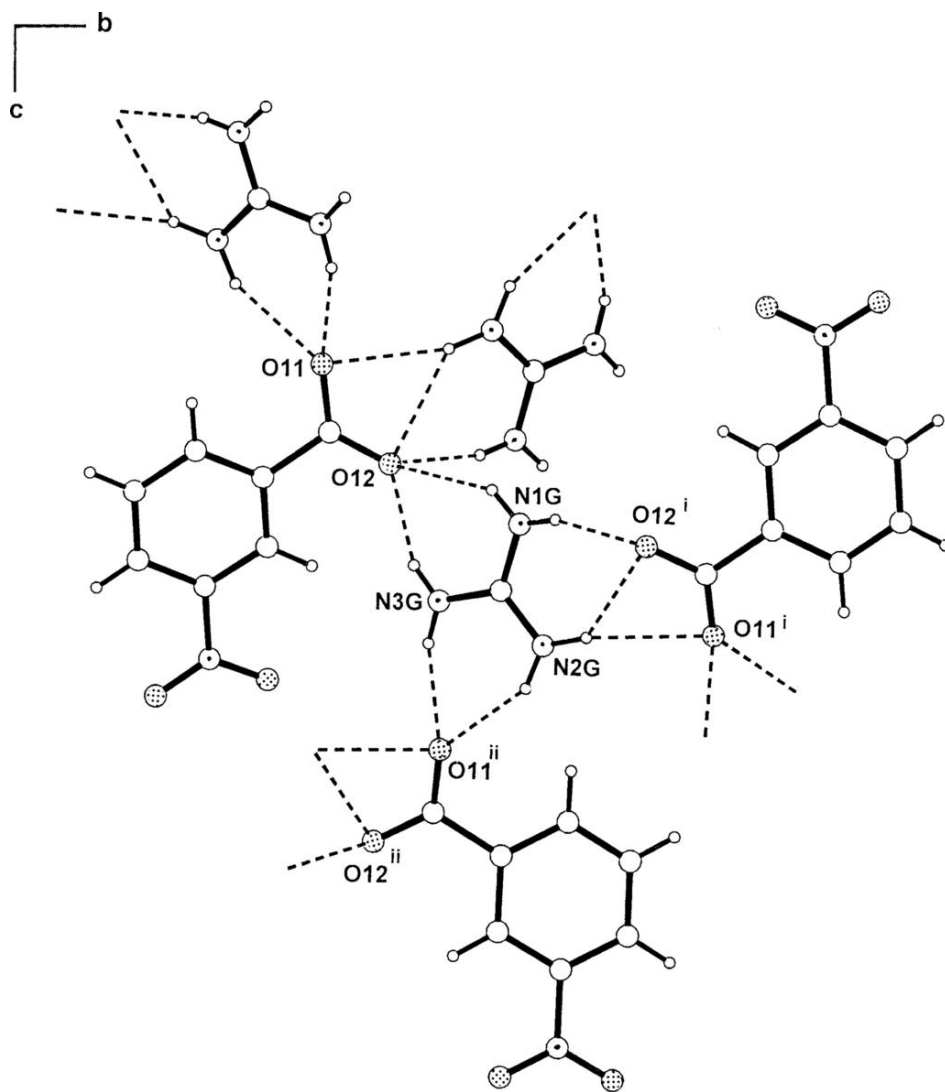


Fig. 3

