organic compounds

(2,4,6-Trinitrophenyl)guanidine

Graham Smith,[a]* Urs D. Wermuth[b] and Jonathan M. White[c]

[a]School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia, [b]School of Biomolecular and Physical Sciences, Griffith University, Nathan, Queensland 4111, Australia, and [c]BIO-21 Molecular Science and Biotechnology, University of Melbourne, Parkville, Victoria 3052, Australia
Correspondence e-mail: g.smith@qut.edu.au

(2,4,6-Trinitrophenyl)guanidine (picrylguanidine), $C_7H_6N_6O_6$, from the reaction of picrylsulfonic acid with guanidine carbonate, forms a three-dimensional framework structure through extensive hydrogen-bonding interactions, extending the centrosymmetric cyclic $R_2^2(16)$ dimer association which includes duplex $R_2^2(8)$ guanidine N—H···O$_{nitro}$ interactions. The guanidine substituent chain has an *endo* [Ph—N=C(NH$_2$)$_2$] bond sequence rather than the less sterically encumbered *exo* [Ph—NH—C=NH(NH$_2$)] sequence of the tautomeric form. As a result, there is significant bond-angle distortion about C(—N=) of the aromatic ring.

Related literature

For related literature, see: Crocker & Matthews (1911); Goldfarb (1966); Lundgren (1972); Lundgren & Tellgren (1974); Russell & Ward (1997); Smith *et al.* (2006, 2007).
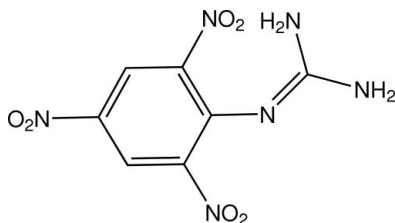
Experimental

Crystal data

$C_7H_6N_6O_6$
M_r = 270.18
Triclinic, $P\bar{1}$
a = 7.6596 (10) Å
b = 7.7316 (10) Å
c = 9.0411 (12) Å
α = 104.045 (3)°
β = 95.004 (2)°
γ = 103.121 (2)°
V = 500.08 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.16 mm^{-1}
T = 130 (2) K
$0.15 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: none
2614 measured reflections
1739 independent reflections
1344 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.083
S = 0.92
1739 reflections
188 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N71—H71A···O41^i	0.85 (2)	2.28 (2)	3.108 (3)	165.7 (18)
N71—H71B···O21^{ii}	0.89 (3)	2.27 (3)	3.155 (2)	173 (2)
N72—H72A···O42^{iii}	0.91 (3)	2.38 (3)	3.180 (3)	147 (2)
N72—H72A···O62^{iv}	0.91 (3)	2.37 (3)	3.058 (3)	132 (2)
N72—H72B···O22^{ii}	0.812 (19)	2.342 (19)	3.139 (2)	168 (2)
C5—H5···O61^v	0.95	2.43	3.339 (3)	159

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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supplementary materials

(2,4,6-Trinitrophenyl)guanidine

G. Smith, U. D. Wermuth and J. M. White

Comment

2,4,6-trinitrobenzenesulfonic acid (picrylsulfonic acid) is a very strong acid which is capable of protonating water, such as is found in the crystalline 'tetrahydrate', which has the formula $C_6H_2N_3O_9S^-$. $H_5O_2^+$. $2H_2O$ [Lundgren, 1972 (X-ray); Lundgren & Tellgren, 1974 (neutron)]. It will therefore readily protonate most Lewis bases, *e.g.* the 1:1 anhydrous salts with guanidine (Russell & Ward, 1997) and quinoline (Smith *et al.*, 2006), and the adduct 2-carboxyquinolinium-picrylsulfon-ate-quinoline-2-carboxylic acid (1/1/1) (Smith *et al.*, 2007). However, certain Lewis base types are capable of displacing the sulfonic acid substituent group (or chloride in the case of picryl chloride) to give amino addition compounds, such as with the three isomeric aminobenzoic acids (Crocker & Matthews, 1911) and with amino acids and proteins (Goldfarb, 1966). The structure of the 4-aminobenzoic acid compound 4-(2,4,6-trinitrophenylanilino)benzoic acid (Smith *et al.*, 2007) is one of very few of this type which have been determined.

The 1:1 stoichiometric reaction of picrylsulfonic acid with guanidine carbonate in methanol was expected to give the previously reported proton-transfer compound guanidinium 2,4,6-trinitrobenzenesulfonate (Russell & Ward, 1997). However, the title compound, the addition compound (2,4,6-trinitrophenyl)guanidine $C_7H_6N_6O_6$ was formed as the only reaction product and the structure is reported here.

The title compound (Fig. 1) is found to have the *endo* [Ph–N=C(NH$_2$)$_2$] bond sequence in the guanidine substituent chain rather than the sterically favoured Ph–NH–C=NH(NH$_2$) sequence of the tautomeric form of picrylguanidine (C·A. registry number 134282–41-1), which has the double bond *exo*. The bond arrangement with the double bond *endo* results in significant distortion in the aromatic ring angles associated with the C1 guanidine substituent group [C2–C1–N1, 128.4 (2) °; C6–C1–N1, 119.56 (19) °; C2–C1–C6, 111.81 (17) °]. The plane of the guanidine double bond is also twisted [torsion angle C1–N1–C71–N72, 151.3 (2) °]. As expected, the nitro groups of the picryl moiety *ortho* to the guanidine substituent are rotated out of the plane of the benzene ring [torsion angles C1–C2–N2–O22, 140.4 (2) Å; C1–C6–N6–O61, 136.2 (2) °], while the *para*-related group is essentially coplanar [C3–C4–N4–O42, −172.1 (2) °].

In the packing of the molecules in the unit cell, all guanidine protons give hydrogen-bonding associations with nitro-O acceptors (Table 1). The basic intermolecular interaction provides a centrosymmetric cyclic $R_2^2(16)$ dimer unit (Fig. 2) which incorporates duplex cyclic $R_2^2(8)$ guanidine *N–H*⋯O$_{nitro}$ group associations [N71,N72⋯O41^{ii},O42^{ii}: symmetry code; (ii) −x + 1, −y, −z + 1]. The overall result is a three-dimensional framework structure. (Fig. 3).

Experimental

The title compound was synthesized by heating together 1 mmol quantities of 2,4,6-trinitrobenzenesulfonic acid (picryl-sulfonic acid) and guanidine carbonate in 50 ml of methanol under reflux for 10 minutes. This reaction is analogous to the reaction of picryl chloride with the isomeric aminobenzoic acids (Crocker & Matthews, 1911) to give the picrylaminoben-

supplementary materials

zoic acids. After concentration to *ca* 30 ml, partial room temperature evaporation of the hot-filtered solution gave a small quantity of pale yellow short crystal prisms of (I).

Refinement

The H atoms bonded to N were located by difference methods and its positional and isotropic displacement parameters were refined. The aromatic ring H atoms were included in the refinement in calculated positions (C—H = 0.95 Å) using a riding model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.
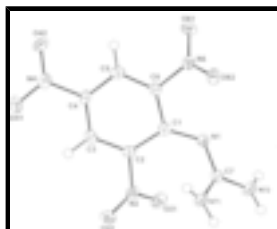
Figures

Fig. 1. Molecular configuration and atom naming scheme (I). Displacement ellipsoids are drawn at the 50% probability level.
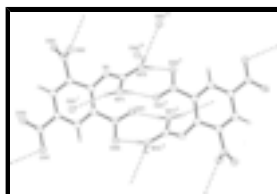
Fig. 2. The cyclic $R_2^2(16)$ hydrogen-bonded dimer incorporating duplex $R_2^2(8)$ *N–H⋯*O$_{nitro}$ associations between centrosymmetrically related molecule pairs in the structure of (I), together with other extending interactions shown as dashed lines. For symmetry codes, see Table 1.
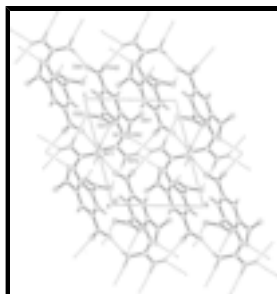
Fig. 3. The three-dimensional framework structure of (I) viewed down the *a* cell direction.

(2,4,6-Trinitrophenyl)guanidine

Crystal data

$C_7H_6N_6O_6$	$Z = 2$
$M_r = 270.18$	$F_{000} = 276$
Triclinic, $P\bar{1}$	$D_x = 1.794$ Mg m^{-3}
Hall symbol: -P 1	Mo *K*α radiation λ = 0.71073 Å
$a = 7.6596$ (10) Å	Cell parameters from 870 reflections
$b = 7.7316$ (10) Å	θ = 2.4–26.8°
$c = 9.0411$ (12) Å	μ = 0.16 mm^{-1}
α = 104.045 (3)°	$T = 130$ (2) K

$\beta = 95.004\ (2)°$

$\gamma = 103.121\ (2)°$

$V = 500.08\ (11)\ \text{Å}^3$

Block, pale yellow

$0.15 \times 0.10 \times 0.10$ mm

Data collection

Bruker CCD area-detector diffractometer	1344 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{\text{int}} = 0.055$
Monochromator: graphite	$\theta_{\text{max}} = 25.0°$
$T = 130(2)$ K	$\theta_{\text{min}} = 2.4°$
φ and ω scans	$h = -9 \rightarrow 9$
Absorption correction: none	$k = -8 \rightarrow 9$
2614 measured reflections	$l = -9 \rightarrow 10$
1739 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.083$	$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.92$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1739 reflections	$\Delta\rho_{\text{max}} = 0.22$ e Å^{-3}
188 parameters	$\Delta\rho_{\text{min}} = -0.21$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	y	z	$U_{\text{iso}}*/U_{\text{eq}}$
O21	0.55099 (19)	0.2258 (2)	0.77212 (16)	0.0256 (5)
O22	0.5482 (2)	−0.0210 (2)	0.84817 (16)	0.0266 (5)
O41	1.0096 (2)	0.1267 (2)	1.29934 (15)	0.0252 (6)

O42	1.2715 (2)	0.3153 (2)	1.30851 (16)	0.0257 (5)
O61	1.3738 (2)	0.5820 (2)	0.86527 (16)	0.0238 (5)
O62	1.2606 (2)	0.3618 (2)	0.65498 (16)	0.0230 (5)
N1	0.8963 (2)	0.3241 (2)	0.66327 (19)	0.0188 (6)
N2	0.6276 (2)	0.1290 (3)	0.83048 (19)	0.0195 (6)
N4	1.1174 (3)	0.2305 (2)	1.24375 (19)	0.0198 (6)
N6	1.2622 (2)	0.4378 (2)	0.79090 (19)	0.0182 (6)
N71	0.7296 (3)	0.0290 (3)	0.5177 (2)	0.0202 (7)
N72	0.6838 (3)	0.2908 (3)	0.4587 (2)	0.0246 (7)
C1	0.9402 (3)	0.2847 (3)	0.7955 (2)	0.0170 (7)
C2	0.8224 (3)	0.1947 (3)	0.8841 (2)	0.0167 (7)
C3	0.8779 (3)	0.1727 (3)	1.0261 (2)	0.0175 (7)
C4	1.0577 (3)	0.2486 (3)	1.0925 (2)	0.0160 (7)
C5	1.1831 (3)	0.3402 (3)	1.0166 (2)	0.0176 (7)
C6	1.1241 (3)	0.3516 (3)	0.8732 (2)	0.0155 (7)
C7	0.7699 (3)	0.2148 (3)	0.5494 (2)	0.0187 (7)
H3	0.79440	0.10670	1.07740	0.0210*
H5	1.30590	0.39310	1.06320	0.0210*
H71A	0.810 (3)	−0.016 (3)	0.553 (2)	0.033 (8)*
H71B	0.658 (3)	−0.040 (3)	0.431 (3)	0.033 (7)*
H72A	0.694 (3)	0.414 (4)	0.486 (3)	0.041 (8)*
H72B	0.612 (3)	0.231 (3)	0.382 (2)	0.015 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O21	0.0228 (9)	0.0305 (10)	0.0241 (9)	0.0108 (8)	−0.0001 (7)	0.0059 (7)
O22	0.0240 (9)	0.0245 (9)	0.0258 (9)	−0.0042 (7)	0.0026 (7)	0.0066 (7)
O41	0.0292 (10)	0.0291 (10)	0.0230 (9)	0.0093 (8)	0.0092 (7)	0.0141 (7)
O42	0.0211 (9)	0.0325 (10)	0.0204 (9)	0.0054 (8)	−0.0037 (7)	0.0050 (7)
O61	0.0212 (9)	0.0190 (9)	0.0266 (9)	−0.0002 (7)	0.0022 (7)	0.0032 (7)
O62	0.0282 (9)	0.0250 (9)	0.0171 (8)	0.0093 (7)	0.0070 (7)	0.0047 (7)
N1	0.0189 (10)	0.0173 (10)	0.0181 (10)	0.0016 (8)	−0.0020 (8)	0.0056 (8)
N2	0.0201 (10)	0.0221 (11)	0.0146 (10)	0.0051 (9)	0.0025 (8)	0.0021 (8)
N4	0.0243 (11)	0.0198 (10)	0.0185 (10)	0.0113 (9)	0.0043 (9)	0.0053 (8)
N6	0.0175 (10)	0.0200 (11)	0.0194 (10)	0.0078 (9)	0.0028 (8)	0.0070 (8)
N71	0.0218 (12)	0.0192 (11)	0.0176 (11)	0.0041 (9)	−0.0024 (9)	0.0040 (9)
N72	0.0289 (12)	0.0200 (12)	0.0206 (12)	0.0033 (10)	−0.0075 (10)	0.0042 (10)
C1	0.0222 (13)	0.0123 (11)	0.0158 (11)	0.0062 (10)	0.0027 (9)	0.0007 (9)
C2	0.0170 (12)	0.0130 (11)	0.0180 (12)	0.0036 (9)	0.0013 (9)	0.0013 (9)
C3	0.0226 (13)	0.0124 (11)	0.0195 (12)	0.0063 (10)	0.0063 (10)	0.0050 (9)
C4	0.0228 (13)	0.0148 (11)	0.0116 (11)	0.0083 (10)	0.0025 (9)	0.0024 (9)
C5	0.0166 (12)	0.0149 (11)	0.0191 (12)	0.0049 (9)	0.0005 (9)	0.0004 (9)
C6	0.0201 (12)	0.0121 (11)	0.0152 (11)	0.0052 (9)	0.0046 (9)	0.0037 (9)
C7	0.0183 (12)	0.0217 (13)	0.0171 (12)	0.0047 (10)	0.0041 (9)	0.0068 (10)

Geometric parameters (Å, °)

O21—N2	1.233 (3)	N71—H71B	0.89 (3)

O22—N2	1.236 (3)	N71—H71A	0.85 (2)
O41—N4	1.243 (2)	N72—H72A	0.91 (3)
O42—N4	1.228 (3)	N72—H72B	0.812 (19)
O61—N6	1.237 (2)	C1—C2	1.432 (3)
O62—N6	1.224 (2)	C1—C6	1.437 (3)
N1—C1	1.337 (3)	C2—C3	1.379 (3)
N1—C7	1.321 (3)	C3—C4	1.385 (3)
N2—C2	1.459 (3)	C4—C5	1.392 (3)
N4—C4	1.453 (3)	C5—C6	1.365 (3)
N6—C6	1.475 (3)	C3—H3	0.9500
N71—C7	1.351 (3)	C5—H5	0.9500
N72—C7	1.330 (3)		
C1—N1—C7	124.54 (18)	N2—C2—C1	120.30 (17)
O21—N2—O22	123.64 (17)	N2—C2—C3	115.16 (19)
O21—N2—C2	118.8 (2)	C1—C2—C3	124.4 (2)
O22—N2—C2	117.56 (18)	C2—C3—C4	118.7 (2)
O41—N4—O42	123.57 (17)	C3—C4—C5	121.37 (18)
O41—N4—C4	117.74 (19)	N4—C4—C5	119.2 (2)
O42—N4—C4	118.68 (18)	N4—C4—C3	119.42 (19)
O61—N6—O62	124.34 (16)	C4—C5—C6	118.0 (2)
O61—N6—C6	117.29 (16)	N6—C6—C5	116.8 (2)
O62—N6—C6	118.37 (16)	N6—C6—C1	117.58 (16)
C7—N71—H71B	119.9 (16)	C1—C6—C5	125.6 (2)
H71A—N71—H71B	117 (2)	N71—C7—N72	118.72 (19)
C7—N71—H71A	116.2 (15)	N1—C7—N71	122.7 (2)
H72A—N72—H72B	116 (2)	N1—C7—N72	118.5 (2)
C7—N72—H72A	120.5 (16)	C2—C3—H3	121.00
C7—N72—H72B	123.2 (17)	C4—C3—H3	121.00
N1—C1—C6	119.56 (19)	C4—C5—H5	121.00
N1—C1—C2	128.4 (2)	C6—C5—H5	121.00
C2—C1—C6	111.81 (17)		
C7—N1—C1—C2	−38.7 (3)	N1—C1—C2—N2	1.5 (3)
C7—N1—C1—C6	147.8 (2)	C2—C1—C6—N6	176.51 (18)
C1—N1—C7—N72	151.3 (2)	N1—C1—C2—C3	−174.5 (2)
C1—N1—C7—N71	−31.4 (3)	C2—C1—C6—C5	−2.6 (3)
O21—N2—C2—C1	−40.4 (3)	C6—C1—C2—N2	175.47 (19)
O22—N2—C2—C1	140.4 (2)	N1—C1—C6—C5	172.0 (2)
O22—N2—C2—C3	−43.1 (3)	N1—C1—C6—N6	−9.0 (3)
O21—N2—C2—C3	136.0 (2)	C6—C1—C2—C3	−0.6 (3)
O41—N4—C4—C3	9.1 (3)	C1—C2—C3—C4	2.9 (3)
O41—N4—C4—C5	−170.2 (2)	N2—C2—C3—C4	−173.4 (2)
O42—N4—C4—C5	8.6 (3)	C2—C3—C4—C5	−2.2 (3)
O42—N4—C4—C3	−172.1 (2)	C2—C3—C4—N4	178.5 (2)
O62—N6—C6—C5	134.5 (2)	N4—C4—C5—C6	178.6 (2)
O61—N6—C6—C5	−44.7 (3)	C3—C4—C5—C6	−0.7 (3)
O61—N6—C6—C1	136.2 (2)	C4—C5—C6—C1	3.3 (4)
O62—N6—C6—C1	−44.7 (3)	C4—C5—C6—N6	−175.84 (19)

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N71—H71A$\cdots$O41[i]	0.85 (2)	2.28 (2)	3.108 (3)	165.7 (18)
N71—H71B$\cdots$O21[ii]	0.89 (3)	2.27 (3)	3.155 (2)	173 (2)
N72—H72A$\cdots$O42[iii]	0.91 (3)	2.38 (3)	3.180 (3)	147 (2)
N72—H72A$\cdots$O62[iv]	0.91 (3)	2.37 (3)	3.058 (3)	132 (2)
N72—H72B$\cdots$O22[ii]	0.812 (19)	2.342 (19)	3.139 (2)	168 (2)
C5—H5$\cdots$O61[v]	0.95	2.43	3.339 (3)	159

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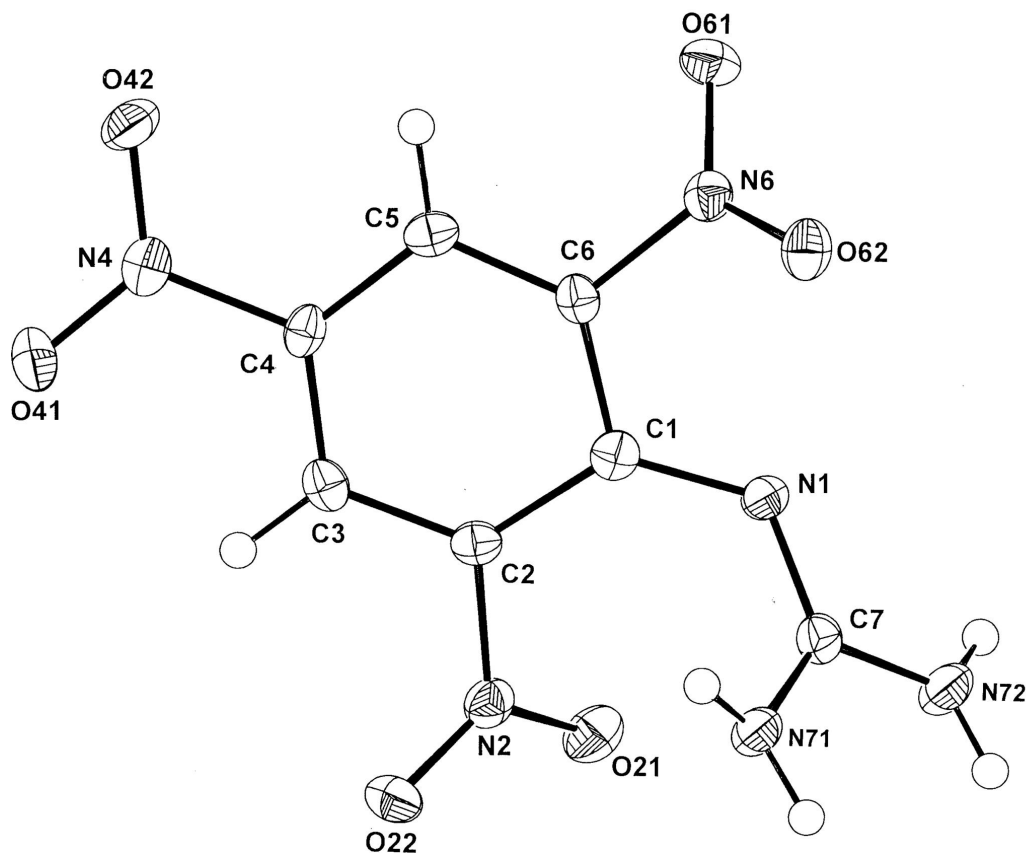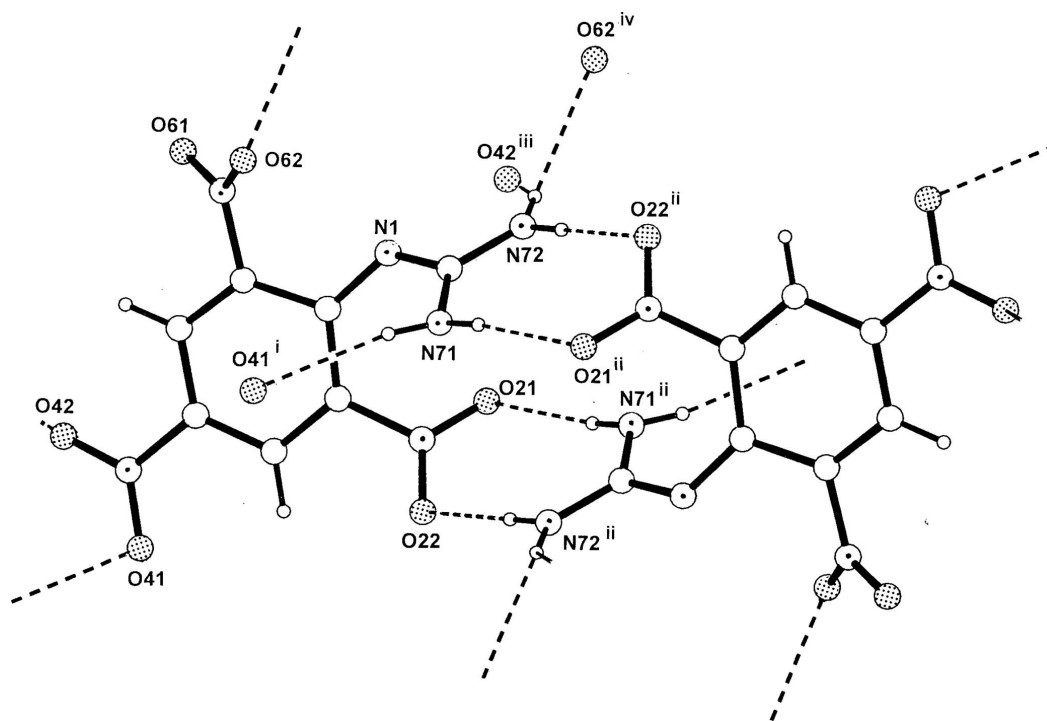
Fig. 1

Fig. 2

Fig. 3