Acta Cryst. (1996). C**52**, 2865-2868

2-Methyl-3-phenyl-2,5-dihydro-1,2,4-triazin-6(1*H*)-one Methanol Solvate and 4-Methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one

David J. Collins,[a] Timothy C. Hughes,[b] Wynona M. Johnson[b] and Maureen F. Mackay[c]

[a]*Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168,* [b]*CSIRO, Division of Chemicals and Polymers, Private Bag 10, South Clayton MDC, Victoria, Australia 3169, and* [c]*School of Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083. E-mail: xraymm2@lure.latrobe.edu.au*

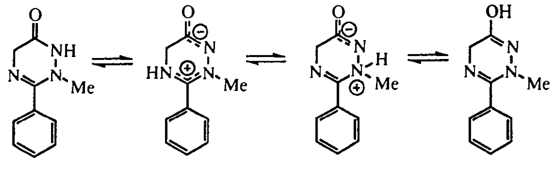
(*Received 4 April 1996; accepted 24 June 1996*)

Abstract

Tautomeric detail in the two title triazinones has been accurately defined. 2-Methyl-3-phenyl-2,5-dihydro-1,2,4-triazin-6(1*H*)-one methanol solvate, $C_{10}H_{11}N_3O.CH_4O$, was found to adopt a zwitterionic form with a dihedral angle between the mean planes of the dihydrotriazinone ring (r.m.s. deviation 0.12 Å) and the phenyl ring of 44.5 (2)°. In the crystal, the molecules are linked by intermolecular hydrogen bonds between the protonated ring-N atom at position 4 and the carbonyl-O atom. 4-Methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one, $C_{10}H_{11}N_3O$, adopts a non-ionic tautomeric form. The dihedral angle between the mean planes of the dihydrotriazinone ring (r.m.s. deviation 0.15 Å) and the phenyl ring is 33.7 (1)°. The molecules in the crystal are linked into dimers by hydrogen bonds between the protonated ring-N atom at position 1 and the carbonyl-O atom.

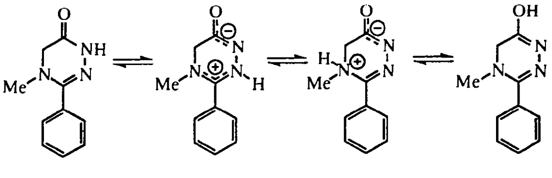
Comment

2-Methyl-3-phenyl-2,5-dihydro-1,2,4-triazin-6(1*H*)-one, (1), which has unusual physical properties which could not be explained by structure (1*a*), was found to adopt the zwitterionic form (1*b*). A perspective view of the molecule is given in Fig. 1(*a*). Atoms N1, N2, C3, N4 and C6 are coplanar to within 0.083 (4) Å with the Csp^3 atom, C5, and the exocyclic atoms O6, C13 and C7 lying 0.438 (4), −0.115 (4), 0.321 (5) and −0.243 (5) Å, respectively, from the mean plane. In 3-(2-hydroxyphenyl)-5,5-dimethyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (Magirius, Linden & Heimgartner, 1993), C5 lies 0.541 (1) Å from the plane of the other tetrahydrotriazinone ring atoms [which are coplanar to within 0.088 (2) Å] with the carbonyl O atom −0.102 (2) Å out of the plane. A similar situation is also observed in 1,3-diphenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (Hajjem, Baccar & Kallel, 1988). In this structure, five of the six dihydrotriazinone ring atoms are coplanar to within 0.058 (4) Å with C5 lying −0.250 (4) and O6 −0.027 (3) Å from the mean plane of the heterocycle; the dihedral angle between the dihydrotriazinone ring plane (r.m.s. deviation 0.079 Å) and the phenyl ring attachment at C3 is only 7.0 (3)°. Interestingly, in compound (1) the lengths of the N2—C3 and C3—N4 bonds are similar [1.322 (4) and 1.312 (4) Å, respectively], and are much shorter than the single N4—C5 bond [1.475 (4) Å]. These two C—N bond lengths and the C6—N1 bond [1.308 (4) Å] are thus indicative of significant double-bond character. The C6—O6 bond [1.268 (4) Å] is longer than the usual ketonic bond and thus attests to some single-bond character. The endocyclic angles subtended at the N atoms range from 116.6 (3) to 122.7 (3)° and are typical of such systems. The 2-methyl-3-phenyldihydrotriazinone moiety was found to be deprotonated at the ring-N atom at position 1, and protonated at the ring-N atom at position 4. This, and the dimensions in the dihydrotriazinone system show that the 2-methyl-3-phenyl structure adopts the tautomeric form (1*b*) in the crystals.



(1*a*) (1*b*) (1*c*) (1*d*)

4-Methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one, (2), adopts the tautomeric non-ionic form (2*a*) (see scheme below) illustrated in Fig. 1(*b*). Atoms N1, N2, C3, N4 and C6 are coplanar to within 0.137 (3) Å with C5 and the exocyclic atoms O6, C7 and C13 lying −0.465 (2), 0.024 (2), 0.127 (3) and 0.571 (3) Å, respectively, from the plane. The dimensions in the dihydrotriazinone ring are very similar to those reported for 1,3-diphenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (Hajjem, Baccar & Kallel, 1988) which adopts an analogous tautomeric form. In (2), the single N1—N2 bond is 1.405 (2) Å and the N2—C3 double bond is 1.296 (2) Å while the N1—C6 and N3—C4 bonds of 1.332 (2) and 1.364 (2) Å, respectively, are significantly shorter than the single N4—C5 bond of 1.451 (2) Å. This is no doubt a consequence of conjugation in the heterocycle as already noted for the 1,3-diphenyl analogue.



(2*a*) (2*b*) (2*c*) (2*d*)

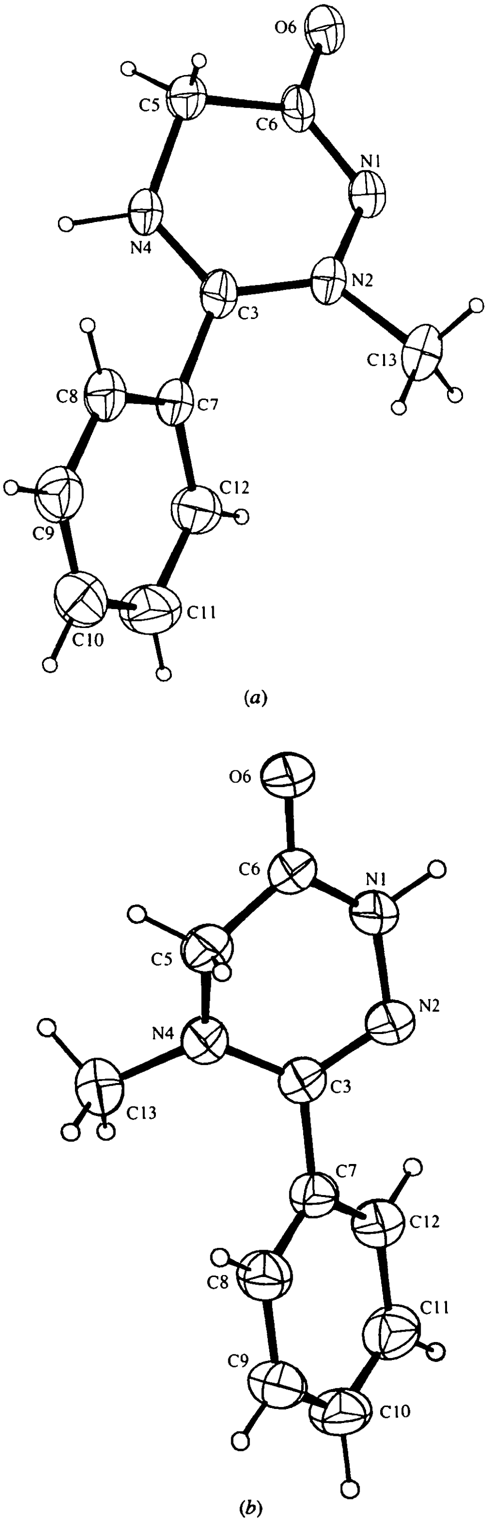


Fig. 1. Perspective views of the molecular structures including the atom numbering: (*a*) compound (1) with displacement ellipsoids at the 30% probability level; (*b*) compound (2) with displacement ellipsoids at the 50% probability level. H atoms are denoted by spheres of arbitrary radius.

The crystal packing in crystals of (1) is illustrated in Fig. 2(*a*). Intermolecular hydrogen bonds (in which the ring-N atom, N4, donates its proton to the carbonyl-O atom of an adjacent molecule related by a twofold screw axis) link the dihydrotriazinone molecules into infinite spirals along the [001] direction in the crystal. The N4···O6(1/2 − *x*, 1−*y*, −1/2+*z*), N4—H4 and H4···O6 distances are 2.802 (4), 0.95 (5) and 1.85 (5) Å, respectively, with an N4—H4···O6 angle of 175 (3)°. Each methanol molecule is hydrogen bonded to a carbonyl-O atom by interactions in which the hydroxyl group of the former donates its proton also to the carbonyl-O atom, the OM1···O6 distance being 2.736 (4) Å.

The crystal packing for (2) is illustrated in Fig. 2(*b*). Intermolecular hydrogen bonds [graph set $R_2^2(8)$; Etter, 1990] in which N2 donates its proton to the carbonyl-O atom, link the molecules into dimers across inversion centres. The N1···O6(1 −*x*, 1−*y*, 2−*z*) and N1—H1, H1···O6 distances are 2.856 (2), 0.97 (2) and 1.90 (3) Å, respectively, with an N1—H1···O6 angle of 168.2 (2)°.

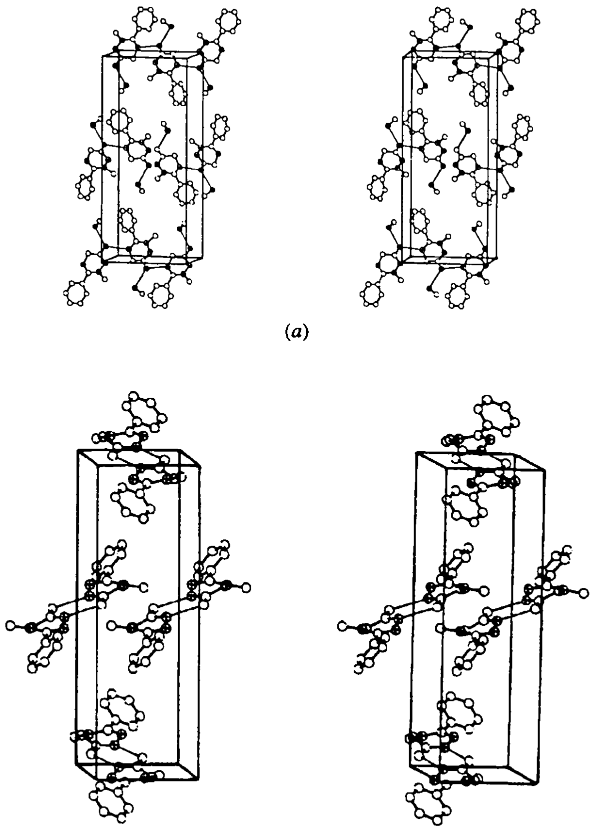


Fig. 2. Stereoviews of the the crystal packings: (*a*) methanol adduct of compound (1) projected along **a** with the *b* axis vertical; (*b*) compound (2) viewed down **a** with the *c* axis vertical.

Experimental

Compound (1) was prepared by the hydrogenolysis and subsequent cyclization of ethyl *N*-[2(benzyloxycarbonyl)-1-methylhydrazino(phenyl)methylene]glycinate (Collins, Hughes & Johnson, 1996). Recrystallization from methanol yielded crystals of the methanol solvate suitable for an X-ray study. As the crystals were unstable in air, a crystal fragment was cut under Nujol and sealed in a Lindeman glass tube for the data collection.

Compound (2) was prepared by cycloaddition of hydrazine hydrate with ethyl *N*-thiobenzoylsarcosinate (Collins, Hughes & Johnson, 1996). Recrystallization from dichloromethane afforded air-stable crystals that were suitable for X-ray analysis. Recrystallization from water yielded identical unsolvated crystals.

Compound (1)

Crystal data

$C_{10}H_{11}N_3O.CH_4O$
$M_r = 221.3$
Orthorhombic
Pbca
$a = 8.856\ (1)$ Å
$b = 24.985\ (2)$ Å
$c = 10.507\ (1)$ Å
$V = 2324.9\ (4)$ Å^3
$Z = 8$
$D_x = 1.264$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 30 reflections
$\theta = 16$–$33°$
$\mu = 0.73$ mm^{-1}
$T = 291\ (2)$ K
Regular prism
0.49 × 0.41 × 0.38 mm
Colourless

Data collection

Rigaku AFC diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (*SHELX*76; Sheldrick, 1976)
$T_{\min} = 0.726$, $T_{\max} = 0.802$
1307 measured reflections
1307 independent reflections

1087 observed reflections $[I > 2\sigma(I)]$
$\theta_{\max} = 65°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 28$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 100 reflections intensity decay: <12%%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR[F^2 > 2\sigma(F^2)] = 0.131$
$S = 1.083$
1307 reflections
190 parameters
H atoms of methanol not located. Other H atoms refined with common $U_{\rm iso}$ = 0.091 (4) Å
$w = 1/[\sigma^2(F_o^2) + (0.0944P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.090$

$\Delta\rho_{\max} = 0.217$ e Å^{-3}
$\Delta\rho_{\min} = -0.166$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0035 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1	0.3175 (3)	0.52764 (10)	0.4119 (2)	0.0554 (8)
N2	0.4021 (3)	0.56824 (11)	0.3497 (2)	0.0542 (8)
C3	0.3999 (4)	0.57497 (13)	0.2249 (3)	0.0522 (9)
N4	0.3424 (4)	0.53732 (11)	0.1525 (2)	0.0565 (9)
C5	0.3149 (6)	0.48323 (14)	0.2039 (3)	0.0606 (11)
C6	0.2714 (4)	0.48771 (13)	0.3414 (3)	0.0517 (9)
O6	0.1916 (3)	0.45062 (9)	0.3889 (2)	0.0636 (8)
C7	0.4519 (4)	0.62547 (13)	0.1643 (3)	0.0504 (9)
C8	0.5515 (5)	0.6224 (2)	0.0621 (3)	0.0605 (10)
C9	0.5974 (5)	0.6685 (2)	0.0001 (4)	0.0688 (11)
C10	0.5430 (6)	0.7168 (2)	0.0393 (4)	0.0817 (14)
C11	0.4444 (6)	0.7212 (2)	0.1412 (4)	0.0829 (14)
C12	0.3972 (5)	0.67499 (15)	0.2032 (4)	0.0656 (11)
C13	0.4859 (5)	0.6010 (2)	0.4397 (4)	0.0677 (12)
OM1	0.1705 (4)	0.35671 (10)	0.2561 (2)	0.0777 (9)
CM1	0.2712 (7)	0.3266 (2)	0.3294 (5)	0.0844 (14)

Table 2. *Selected geometric parameters (Å, °) for (1)*

N1—C6	1.308 (4)	C3—C7	1.486 (4)
N1—N2	1.421 (4)	N4—C5	1.475 (4)
N2—C3	1.322 (4)	C5—C6	1.499 (4)
N2—C13	1.455 (4)	C6—O6	1.268 (4)
C3—N4	1.312 (4)	OM1—CM1	1.398 (5)
C6—N1—N2	116.6 (3)	C3—N4—C5	120.6 (3)
C3—N2—N1	122.7 (3)	N4—C5—C6	109.1 (3)
C3—N2—C13	125.5 (3)	O6—C6—N1	120.6 (3)
N1—N2—C13	111.8 (3)	O6—C6—C5	117.9 (3)
N4—C3—N2	119.3 (3)	N1—C6—C5	121.5 (3)
N4—C3—C7	118.7 (3)	C12—C7—C3	121.4 (3)
N2—C3—C7	121.9 (3)	C8—C7—C3	118.7 (3)
N1—N2—C3—N4	−13.7 (3)	C6—N1—N2—C3	19.1 (4)
N2—C3—N4—C5	−14.8 (5)	N4—C3—N2—C13	167.8 (3)
C3—N4—C5—C6	33.5 (4)	C7—C3—N2—C13	−16.0 (5)
N4—C5—C6—N1	−27.7 (4)	N2—N1—C6—O6	−178.0 (3)
C5—C6—N1—N2	4.1 (4)	N2—C3—C7—C12	−51.8 (5)

Compound (2)

Crystal data

$C_{10}H_{11}N_3O$
$M_r = 189.22$
Monoclinic
$P2_1/n$
$a = 6.6707\ (5)$ Å
$b = 7.0151\ (5)$ Å
$c = 20.722\ (1)$ Å
$\beta = 98.71\ (1)°$
$V = 958.5\ (1)$ Å^3
$Z = 4$
$D_x = 1.311$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 20$–$32°$
$\mu = 0.722$ mm^{-1}
$T = 291\ (2)$ K
Regular prism
0.33 × 0.26 × 0.23 mm
Colourless

Data collection

Rigaku AFC diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (*SHELX*76; Sheldrick, 1976)
$T_{\min} = 0.832$, $T_{\max} = 0.886$
1743 measured reflections
1594 independent reflections
1371 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.016$
$\theta_{\max} = 65°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 24$
3 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR[F^2 > 2\sigma(F^2)] = 0.093$
$S = 1.172$
1594 reflections
174 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.2474P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.133$ e Å^{-3}
$\Delta\rho_{\min} = -0.225$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0495 (25)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
N1	0.2477 (2)	0.4287 (2)	0.95301 (7)	0.0445 (4)
N2	0.0693 (2)	0.4607 (2)	0.90889 (7)	0.0420 (4)
C3	−0.0334 (2)	0.3081 (2)	0.89075 (8)	0.0378 (4)
N4	0.0351 (2)	0.1289 (2)	0.90749 (7)	0.0474 (4)
C5	0.2532 (3)	0.1024 (3)	0.92074 (10)	0.0498 (5)
C6	0.3519 (2)	0.2660 (2)	0.95940 (8)	0.0432 (4)
O6	0.5186 (2)	0.2507 (2)	0.99457 (7)	0.0606 (4)
C7	−0.2319 (2)	0.3370 (2)	0.84853 (7)	0.0379 (4)
C8	−0.2913 (3)	0.2221 (3)	0.79429 (8)	0.0449 (4)
C9	−0.4750 (3)	0.2534 (3)	0.75436 (9)	0.0501 (5)
C10	−0.6002 (3)	0.3993 (3)	0.76856 (9)	0.0535 (5)
C11	−0.5416 (3)	0.5159 (3)	0.82187 (9)	0.0503 (5)
C12	−0.3580 (2)	0.4850 (2)	0.86192 (8)	0.0430 (4)
C13	−0.0951 (3)	−0.0368 (3)	0.90918 (11)	0.0546 (5)

Table 4. *Selected geometric parameters (Å, °) for (2)*

N1—C6	1.332 (2)	N4—C5	1.451 (2)
N1—N2	1.405 (2)	N4—C13	1.455 (2)
N2—C3	1.296 (2)	C5—C6	1.494 (2)
C3—N4	1.364 (2)	C6—O6	1.238 (2)
C3—C7	1.486 (2)		
C6—N1—N2	125.4 (1)	C5—N4—C13	118.5 (2)
C3—N2—N1	114.5 (1)	N4—C5—C6	110.5 (1)
N2—C3—N4	123.1 (1)	O6—C6—N1	122.8 (2)
N2—C3—C7	116.3 (1)	O6—C6—C5	122.1 (2)
N4—C3—C7	120.6 (1)	N1—C6—C5	115.1 (1)
C3—N4—C5	117.0 (1)	C3—C7—C8	121.1 (1)
C3—N4—C13	124.4 (1)	C3—C7—C12	119.8 (1)
N1—N2—C3—N4	−6.5 (3)	C6—N1—N2—C3	24.5 (4)
N2—C3—N4—C5	−26.7 (5)	N2—C3—N4—C13	157.0 (3)
C3—N4—C5—C6	41.3 (4)	C7—C3—N4—C13	−24.5 (5)
N4—C5—C6—N1	−24.6 (4)	N2—N1—C6—O6	172.9 (3)
C5—C6—N1—N2	−7.0 (4)	N2—C3—C7—C12	−41.2 (4)

For both compounds, data collection: *AFC/MSC Software* (Rigaku Corporation, 1988); cell refinement: *AFC/MSC Software*; data reduction: *AFC/MSC Software*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson,1976); software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Collins, D. J., Hughes, T. C. & Johnson, W. M. (1996). *Aust. J. Chem.* In the press.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Hajjem, B., Baccar, B. & Kallel, A. (1988). *Acta Cryst.* C**44**, 1440–1442.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Magirius, F., Linden, A. & Heimgartner, H. (1993). *Helv. Chim. Acta*, **76**, 1980–20
Rigaku Corporation (1988). *AFC/MSC. Data Collection and Refinement Software*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. University of Cambridge, England.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 2868-2871

p-Nitroaniline–3,5-Dinitromethyl Salicylate (1:1) Co-Crystal

Kin-Shan Huang,† Doyle Britton and Margaret C. Etter‡

Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455, USA. E-mail: huangk@aa.wl.com

(Received 25 January 1996; accepted 2 July 1996)

Abstract

The title compound, $C_6H_6N_2O_2.C_8H_6N_2O_7$, is composed of one molecule of *p*-nitroaniline and one molecule of 3,5-dinitromethyl salicylate. In this co-crystal, both the *p*-nitroaniline and 3,5-dinitromethyl salicylate molecules are nearly planar. These two molecules are almost coplanar with respect to each other, with a dihedral angle of 3.2 (2)° between the two aromatic-ring least-squares planes. The hydroxyl group of the 3,5-dinitromethyl salicylate molecule forms an intramolecular six-membered-ring hydrogen bond to the ester carbonyl-O atom [H8···O1 = 1.74 (4), O8···O1 = 2.547 (4) Å, O8—H8···O1 = 144 (3)°]. The *p*-nitroaniline molecules are aggregated into infinite chains by intermolecular N—H···O hydrogen bonds between one of the amino protons, H1*A*, and one of the nitro-O atoms, O4*B*, of the nitroaniline molecules [H1*A*···O4*B*^{i} = 2.22 (3), N1···O4*B*^{i} = 2.984 (4) Å, N1—H1*A*···O4*B*^{i} = 152 (3)°; symmetry code: (i) $x + \frac{1}{2}, -\frac{1}{2} - y, -\frac{1}{2} + z$]. The

---

† Present address: Pharmaceutical Research, Warner-Lambert Company, 170 Tabor Road, Morris Plains, NJ 07950, USA.
‡ Deceased.