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: *SHELXL93* (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 (Å²) 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 (1)
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: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson,1976); software used to prepare material for publication: *SHELXL93*.

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.

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

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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, H1A, and one of the nitro-O atoms, O4B, of the nitroaniline molecules [H1A···O4B^i = 2.22 (3), N1···O4B^i = 2.984 (4) Å, N1—H1A···O4B^i = 152 (3)°; symmetry code: (i) $x + \frac{1}{2}, -\frac{1}{2} - y, -\frac{1}{2} + z$]. The

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3,5-dinitromethyl salicylate molecules are linked to the nitroaniline chains by multiple intermolecular hydrogen bonds [O8$\cdots$O4B = 2.968 (3) Å, N1$\cdots$O8^i = 3.147 (3) Å and N1$\cdots$O9A^i = 3.008 (4) Å].

Comment

Nitroaniline compounds have long been of interest in non-linear optical (NLO) materials because of their inherently large molecular polarizability (β) (microscopic non-linearity) (Williams, 1984). Hydrogen-bonding interactions have been found to be important in the non-centrosymmetric crystal packing of organic compounds (Zyss, Nicoud & Coquillay, 1984). In addition, hydrogen-bond-directed co-crystallization has been demonstrated to be a useful way of studying the molecular recognition and hydrogen-bonding properties of a class of related host molecules (Etter & Baures, 1988; Etter, Urbanczyk-Lipkowska, Zia-Ebrahimi & Panunto, 1990; Etter & Reutzel, 1991).

In our continuing research on designing NLO materials using hydrogen-bonding interactions (Etter & Frankenbach, 1989; Etter & Huang, 1992), the title compound, (I), was obtained from the co-crystallization of *p*-nitroaniline with 3,5-dinitromethyl salicylate.

(I)
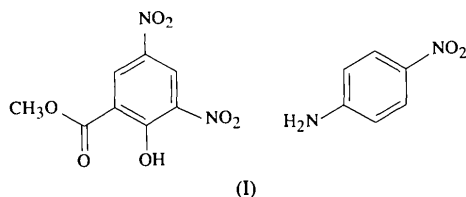
The co-crystal is composed of one molecule of *p*-nitroaniline and one molecule of 3,5-dinitromethyl salicylate. As with the crystal structure of *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961), the *p*-nitroaniline molecule in the co-crystal is nearly planar, with the amine and nitro groups rotated 6 (2) and 0.7 (2)°, respectively, out of the least-squares plane of the aromatic ring. Similarly, the 3,5-dinitromethyl salicylate molecule is nearly planar; the ester group and the two nitro groups at C9 and C11 are rotated 4.4 (2), 10.1 (3) and 7.6 (2)°, respectively, out of the least-squares plane of the aromatic ring. Moreover, these two molecules in the co-crystal are almost coplanar with respect to each other, with a dihedral angle of 3.2 (2)° between the two aromatic-ring least-squares planes. For the *p*-nitroaniline molecule, the C1—N1 bond distance of 1.346 (3) Å is significantly shorter than that of the C4—N4 [1.429 (3) Å], suggesting that the amino group interacts with the aromatic ring to a greater extent than does the nitro group. Hence, the structure of the *p*-nitroaniline molecule is expected to exist in a partial quinonoid resonance form. The partial quinonoid resonance form is also reflected by the shorter bond lengths of C2—C3 [1.361 (3) Å] and C5—C6

[1.371 (4) Å] than those of C1—C2 [1.411 (4) Å], C3—C4 [1.389 (3) Å], C4—C5 [1.391 (3) Å] and C1—C6 [1.407 (4) Å].
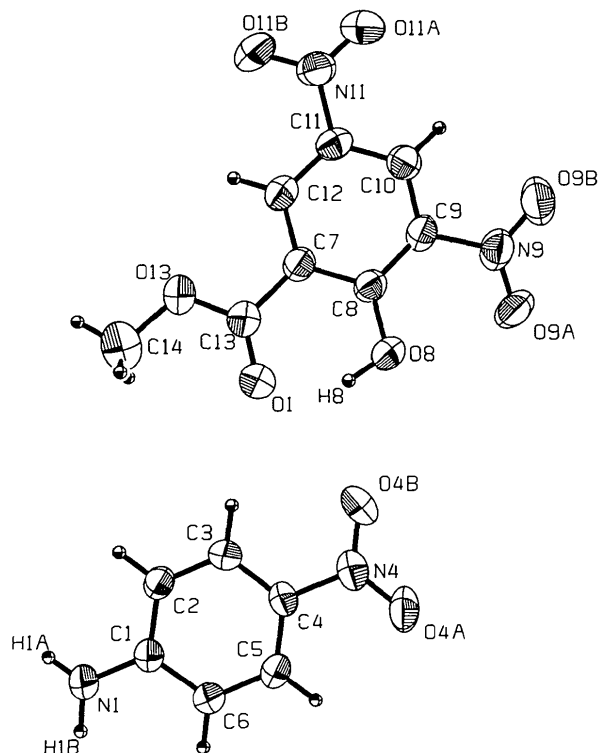

Fig. 1. The molecular structure of the title compound showing displacement ellipsoids at the 50% probability level.

The hydroxyl group of the 3,5-dinitromethyl salicylate molecule is oriented toward the *ortho* methyl ester group rather than the *ortho* nitro group. This conformation enables the hydroxyl group to form an intramolecular six-membered-ring hydrogen bond to the ester carbonyl-O atom, [H8$\cdots$O1 = 1.74 (4), O8$\cdots$O1 = 2.547 (4) Å, O8—H8$\cdots$O1 = 144 (3)°] (Fig. 2 and Table 3). This type of hydrogen-bonding pattern is designated S_1^1(6) [or $S(6)$] according to the Etter notation (Etter, MacDonald & Bernstein, 1990). [This notation indicates the self-cyclic (S) nature of the hydrogen-bonded aggregate, the one proton donor and one proton acceptor (as subscript and superscript, respectively) involved in the bonding, and the ring size (in parentheses).] In this structure, the *p*-nitroaniline molecules are aggregated into infinite chains [C_1^1(8), C = chain] by intermolecular N—H$\cdots$O hydrogen bonds between one of the amino protons, H1A, and one of the nitro-O atoms, O4B, of the nitroaniline molecules [H1$A\cdots$O4B^i = 2.22 (3), N1$\cdots$O4B^i = 2.984 (4) Å, N1—H1$A\cdots$O4B^i = 152 (3)°; symmetry code: (i) $x + \frac{1}{2}, -\frac{1}{2} - y, -\frac{1}{2} + z$]. The 3,5-dinitromethyl salicylate molecules are linked to the nitroaniline chains by multiple intermolecular hydrogen bonds to form a (1:1) co-crystal. The other amino proton, H1B, of the nitroaniline forms bifurcated hydrogen bonds [2D] to the

hydroxy O atom of the salicylate molecules [N1···O8ᶦ = 3.147 (3) Å] and to one of the nitro-O atoms at C9, O9A, of the salicylate molecules [N1···O9Aᶦ = 3.008 (4) Å]. The primary and secondary graph sets for H1B would be N_1 = 2D and N_2 = $R_1^2(6)$, respectively. Finally, the hydroxyl group of the salicylate forms intermolecular O—H···O hydrogen bonds [D] to atom O4B of the nitroaniline molecules [O8···O4B = 2.968 (3) Å].
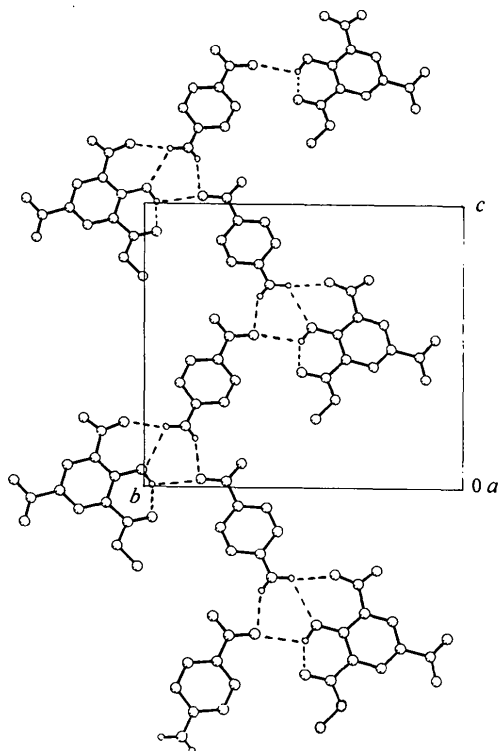

Fig. 2. A packing diagram of the title compound viewed down the *a* axis. Hydrogen bonds are indicated by dashed lines.

Experimental

3,5-Dinitromethyl salicylate was synthesized from 3,5-dinitro-salicylic acid and methanol with sulfuric acid as a catalyst (Clinton & Laskowski, 1948). Crystals of the title compound were prepared by dissolving *p*-nitroaniline and 3,5-dinitro-methyl salicylate in a 1:1 molar ratio in ethyl acetate using slow evaporation methods.

Crystal data

$C_6H_6N_2O_2.C_8H_6N_2O_7$	Mo $K\alpha$ radiation
M_r = 380.27	λ = 0.71073 Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
a = 7.755 (6) Å	θ = 16.0–23.4°
b = 15.352 (4) Å	μ = 0.126 mm⁻¹
c = 13.508 (9) Å	T = 211 K
β = 95.73 (6)°	Prism

V = 1600 (3) Å³	0.60 × 0.60 × 0.45 mm
Z = 4	Yellow
D_x = 1.578 Mg m⁻³	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	R_{int} = 0.031
diffractometer	θ_{max} = 26°
Profile data from ω scans	h = −8 → 8
Absorption correction:	k = 0 → 17
none	l = −15 → 15
6511 measured reflections	3 standard reflections
3271 independent reflections	frequency: 50 min
2270 observed reflections	intensity decay: <1%
[$I > 2\sigma(I)$]	(no correction applied)

Refinement

Refinement on F	Extinction correction:
R = 0.051	secondary extinction
wR = 0.067	Extinction coefficient:
S = 1.80	0.43181 × 10⁻⁶
2270 reflections	Atomic scattering factors
257 parameters	from *International Tables*
$w = 4F^2/\sigma^2(F^2)$	*for X-ray Crystallography*
$(\Delta/\sigma)_{max}$ = 0.01	(1974, Vol. IV, Table
$\Delta\rho_{max}$ = 0.59 e Å⁻³	2.2A)
$\Delta\rho_{min}$ = −0.27 e Å⁻³	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* $(\mathring{A}^2)$

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1	0.2985 (4)	−0.0116 (1)	−0.0684 (2)	6.7 (1)
N1	0.5516 (4)	−0.3857 (2)	−0.2549 (2)	4.5 (1)
C1	0.4730 (3)	−0.3517 (2)	−0.1793 (2)	3.3 (1)
C2	0.4428 (3)	−0.2613 (2)	−0.1736 (2)	3.2 (1)
C3	0.3656 (3)	−0.2270 (2)	−0.0962 (2)	3.3 (1)
O4A	0.1739 (3)	−0.2941 (1)	0.1196 (1)	4.9 (1)
O4B	0.2195 (3)	−0.1659 (1)	0.0645 (2)	5.7 (1)
N4	0.2321 (3)	−0.2457 (2)	0.0583 (2)	3.9 (1)
C4	0.3141 (3)	−0.2816 (2)	−0.0226 (2)	3.2 (1)
C5	0.3400 (4)	−0.3712 (2)	−0.0262 (2)	3.7 (1)
C6	0.4189 (4)	−0.4055 (2)	−0.1039 (2)	3.8 (1)
C7	0.2408 (3)	0.1330 (2)	−0.0222 (2)	3.4 (1)
O8	0.1627 (3)	0.0235 (1)	0.0910 (2)	4.8 (1)
C8	0.1721 (3)	0.1070 (2)	0.0664 (2)	3.5 (1)
O9A	0.0642 (5)	0.0813 (2)	0.2579 (2)	9.3 (2)
O9B	−0.0216 (3)	0.2124 (2)	0.2645 (2)	6.0 (1)
N9	0.0450 (4)	0.1535 (2)	0.2226 (2)	4.6 (1)
C9	0.1150 (3)	0.1727 (2)	0.1279 (2)	3.6 (1)
C10	0.1188 (3)	0.2590 (2)	0.1015 (2)	3.5 (1)
O11A	0.1438 (3)	0.4270 (1)	0.0453 (2)	6.2 (1)
O11B	0.2215 (3)	0.3913 (1)	−0.0977 (2)	6.3 (1)
N11	0.1824 (3)	0.3732 (2)	−0.0152 (2)	4.6 (1)
C11	0.1820 (3)	0.2813 (2)	0.0130 (2)	3.6 (1)
C12	0.2441 (3)	0.2205 (2)	−0.0491 (2)	3.5 (1)
O13	0.3774 (3)	0.0958 (1)	−0.1638 (1)	4.7 (1)
C13	0.3078 (4)	0.0652 (2)	−0.0864 (2)	4.1 (1)
C14	0.4454 (6)	0.0319 (3)	−0.2317 (3)	7.1 (2)

Table 2. *Selected geometric parameters* $(\mathring{A}, °)$

C13—O1	1.208 (3)	C7—C12	1.392 (3)
C13—O13	1.311 (3)	C8—C9	1.406 (4)
C9—N9	1.467 (3)	C10—C11	1.379 (4)
C7—C8	1.416 (4)	C1—N1	1.346 (3)
C7—C13	1.482 (4)	C1—C2	1.411 (4)
C9—C10	1.373 (4)	C2—C3	1.361 (3)

C11—C12	1.373 (4)	C4—C5	1.391 (3)
C4—N4	1.429 (3)	O9A—N9	1.210 (3)
C1—C6	1.407 (4)	O9B—N9	1.210 (3)
C3—C4	1.389 (3)	O11A—N11	1.220 (3)
C5—C6	1.371 (4)	O11B—N11	1.216 (3)
C8—O8	1.328 (3)	O4A—N4	1.230 (3)
C14—O13	1.476 (4)	O4B—N4	1.233 (3)
C11—N11	1.461 (3)		
C13—O13—C14	117.3 (3)	O9A—N9—O9B	122.8 (3)
O9A—N9—C9	119.1 (3)	O9B—N9—C9	118.0 (2)
O11A—N11—O11B	124.0 (2)	O11A—N11—C11	118.2 (3)
O11B—N11—C11	117.9 (2)	C8—C7—C13	118.7 (2)
C12—C7—C13	120.6 (2)	O8—C8—C7	121.2 (2)
O8—C8—C9	121.1 (2)	O1—C13—O13	123.2 (3)
O1—C13—C7	122.4 (3)	O4A—N4—O4B	121.1 (2)
O4A—N4—C4	120.2 (2)	O4B—N4—C4	118.6 (2)
N1—C1—C2	120.9 (2)	N1—C1—C6	120.8 (2)

Table 3. *Hydrogen-bonding geometry* ($\mathring{A}$, °)

D—H$\cdots$A	D—H	H$\cdots$A	D$\cdots$A	D—H$\cdots$A
O8—H8$\cdots$O1	0.92 (4)	1.74 (4)	2.547 (4)	144 (3)
O8—H8$\cdots$O4B	0.92 (4)	2.41 (4)	2.968 (3)	119 (4)
N1—H1A$\cdots$O4B^i	0.83 (3)	2.22 (3)	2.984 (4)	152 (3)
N1—H1B$\cdots$O8^i	0.94 (3)	2.56 (3)	3.147 (3)	121 (4)
N1—H1B$\cdots$O9A^i	0.94 (3)	2.07 (3)	3.008 (4)	172 (3)

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

Atom O9A has an unusually large B_{eq} value, reflecting highly anisotropic displacement parameters. This could be due to disorder, so the anisotropic atom was replaced with two isotropic half atoms. Refinement of this model converged with $R = 0.056$ and $wR = 0.074$, significantly worse than the anisotropic model. We are left with no explanation for this large anisotropy; it does not appear to be due to disorder between two distinct positions.

The non-H atoms were refined anisotropically. All H atoms except H1A, H1B and H8, for which all parameters were refined isotropically, were included in the calculations placed in idealized positions (C—H 0.95 $\mathring{A}$) with $B_{iso} = 1.2B_{eq}$ of the atoms to which they are bonded.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984), *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1232). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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L-Leucyl-L-alanine Dimethyl Sulfoxide Solvate

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Abstract

In the title compound, $C_9H_{18}N_2O_3 \cdot C_2H_6OS$, the dipeptide molecule exists as a zwitterion and the backbone adopts an extended conformation. The peptide unit is *trans* and shows a slight deviation from planarity [$\omega_1 = 174.4$ (3)°]. The leucyl side chain adopts the $t(g^+t)$ conformation. The crystal packing gives rise to channels which are occupied by the disordered DMSO solvent molecules.

Comment

Structural studies on peptides represent an ongoing project in our laboratory aimed at identifying stable peptide conformations for use in models for protein folding. The present study forms part of the work on several Leu-X peptides.

† DCB Contribution No. 873.