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4-Nitroaniline–2,4,6-trimethoxybenzaldehyde (1/1)

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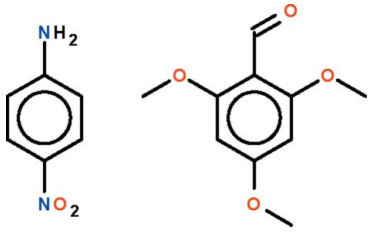
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.049; wR factor = 0.124; data-to-parameter ratio = 12.3.

In the title co-crystal, $C_6H_6N_2O_2.C_{10}H_{12}O_4$, the two components are held together by an N—H···$O_{aldehyde}$ hydrogen bond. Adjacent co-crystals are linked by weaker N—H···O_{nitro} hydrogen bonds, forming a linear chain. The two aromatic rings of the components are aligned at 75.2 (1)°. The crystal studied was a non-merohedral twin with a 24% minor component.

Related literature

For some examples of co-crystals of 4-nitroaniline, see: Bertolasi *et al.* (2001); Dederer & Gieren (1979); Huang *et al.* (1996); Koshima *et al.* (1996); Rashid & Deschamps (2006); Singh *et al.* (2003); Smith *et al.* (1997); Weber (1981); Zaitu *et al.* (1995). For the treatment of non-merohedral twins, see: Spek (2009).



Experimental

Crystal data

$C_6H_6N_2O_2·C_{10}H_{12}O_4$ M_r = 334.32
Monoclinic, $P2_1/c$
a = 7.4409 (11) Å
b = 30.022 (5) Å
c = 6.9400 (11) Å
β = 93.237 (3)°
V = 1547.9 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.15 × 0.10 × 0.05 mm

Data collection

Bruker SMART APEX diffractometer
8127 measured reflections
2722 independent reflections
1834 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.124
S = 1.01
2722 reflections
221 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H12···O1	0.86	2.16	3.016 (3)	172
N1—H11···O5^{i}	0.86	2.50	3.288 (3)	152
N1—H11···O6^{i}	0.86	2.50	3.293 (3)	154

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2271).

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supplementary materials

Acta Cryst. (2010). E**66**, o1765 [**doi:10.1107/S1600536810023664**]

4-Nitroaniline-2,4,6-trimethoxybenzaldehyde (1/1)

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Comment

Aromatic aldehydes readily condense with aromatic amines to yield Schiff bases. However, 2,4,6-trimethoxylbenzaldehyde and 4-nitroaniline reactants did not condense but instead co-crystallized in the attempted synthesis. The condensation probably did not proceed owing to the decreased basicity of the amino group, which is situated opposite the electron-withdrawing nitro group in the aromatic ring. The co-crystal (Scheme I, Fig. 1) has the components linked by an H–N···O hydrogen bond; the two aromatic rings aligned at 75.2 (1) °. Adjacent co-crystals are linked by weaker *N*–*H*···O_{nitro} hydrogen bonds to form a linear chain.

4-Nitroaniline forms a number of co-crystals with other neutral compounds; for their description, see: Bertolasi *et al.* (2001); Dederer & Gieren (1979); Huang *et al.* (1996); Koshima *et al.* (1996); Rashid & Deschamps (2006); Singh *et al.* (2003); Smith *et al.* (1997); Weber (1981); Zaitu *et al.* (1995).

Experimental

2,4, 6-Trimethoxybenzaldehyde (0.50 g, 3.3 mmol) and 4-nitroaniline (0.57 g, 3.3 mmol) were heated in methanol (15 ml) for 5 h. Yellow crystals separated from the cool solution after a day.

Refinement

Carbon- and nitrogen-bound H-atoms were placed in calculated positions [C–H 0.95 to 0.98 Å, N–H 0.86 Å; *U*(H) 1.2 to 1.5U_{eq}(*C*,*N*)] and were included in the refinement in the riding model approximation.

The crystal studied is a non-merohedral twin; the twin law (1 0 0.121, 0 - 1 0, 0 0 - 1) as given by *PLATON* (Spek, 2009) was used to de-twin the diffraction data.

Figures

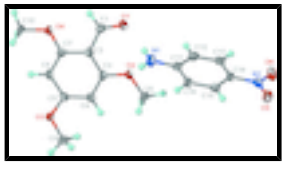


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of the $C_6H_6N_2O_2$–$C_{10}H_{12}O_4$ co-crystal at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

4-Nitroaniline–2,4,6-trimethoxybenzaldehyde (1/1)

Crystal data

$C_6H_6N_2O_2·C_{10}H_{12}O_4$ $F(000) = 704$

M_r = 334.32	D_x = 1.435 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 1019 reflections
a = 7.4409 (11) Å	θ = 2.7–24.4°
b = 30.022 (5) Å	μ = 0.11 mm^{-1}
c = 6.9400 (11) Å	T = 100 K
β = 93.237 (3)°	Prism, yellow
V = 1547.9 (4) Å^3	0.15 × 0.10 × 0.05 mm
Z = 4	

Data collection

Bruker SMART APEX diffractometer	1834 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.059
graphite	θ_{max} = 25.0°, θ_{min} = 1.4°
ω scans	h = −8→8
8127 measured reflections	k = −32→35
2722 independent reflections	l = −8→8

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.049	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.124	H-atom parameters constrained
S = 1.01	$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.141P]$ where $P = (F_o^2 + 2F_c^2)/3$
2722 reflections	$(\Delta/\sigma)_{max}$ = 0.001
221 parameters	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.7019 (2)	0.57392 (6)	0.7861 (3)	0.0238 (5)
O2	0.7670 (2)	0.61120 (6)	0.4418 (2)	0.0182 (4)
O3	1.3371 (2)	0.57367 (6)	0.1850 (2)	0.0203 (4)
O4	1.1646 (2)	0.51253 (6)	0.7725 (2)	0.0176 (4)
O5	0.0363 (2)	0.80574 (6)	0.5273 (3)	0.0266 (5)
O6	−0.0908 (2)	0.74324 (7)	0.4450 (3)	0.0291 (5)
N1	0.6593 (3)	0.67379 (7)	0.7727 (3)	0.0233 (5)
H11	0.7505	0.6884	0.8209	0.028*
H12	0.6631	0.6452	0.7670	0.028*
N2	0.0398 (3)	0.76456 (7)	0.5159 (3)	0.0193 (5)

C1	0.8433 (3)	0.55435 (8)	0.7589 (4)	0.0177 (6)
H1	0.8764	0.5314	0.8482	0.021*
C2	0.9658 (3)	0.56212 (8)	0.6066 (3)	0.0152 (6)
C3	0.9285 (3)	0.59010 (8)	0.4462 (4)	0.0154 (6)
C4	1.0482 (3)	0.59515 (8)	0.3011 (4)	0.0155 (6)
H4	1.0203	0.6140	0.1936	0.019*
C5	1.2098 (3)	0.57189 (8)	0.3175 (4)	0.0157 (6)
C6	1.2542 (3)	0.54410 (8)	0.4744 (4)	0.0170 (6)
H6	1.3662	0.5289	0.4834	0.020*
C7	1.1335 (3)	0.53914 (8)	0.6155 (3)	0.0144 (6)
C8	0.7184 (3)	0.63908 (9)	0.2781 (4)	0.0216 (6)
H8A	0.5983	0.6516	0.2923	0.032*
H8B	0.7179	0.6213	0.1597	0.032*
H8C	0.8061	0.6633	0.2709	0.032*
C9	1.3034 (3)	0.60080 (8)	0.0177 (4)	0.0198 (6)
H9A	1.4039	0.5980	−0.0669	0.030*
H9B	1.2913	0.6320	0.0570	0.030*
H9C	1.1920	0.5910	−0.0516	0.030*
C10	1.3340 (3)	0.48903 (9)	0.7879 (4)	0.0193 (6)
H10A	1.3403	0.4709	0.9054	0.029*
H10B	1.4332	0.5106	0.7934	0.029*
H10C	1.3436	0.4697	0.6751	0.029*
C11	0.5099 (3)	0.69579 (9)	0.7057 (3)	0.0168 (6)
C12	0.3577 (3)	0.67245 (9)	0.6292 (4)	0.0189 (6)
H12A	0.3622	0.6409	0.6183	0.023*
C13	0.2034 (3)	0.69466 (9)	0.5705 (4)	0.0186 (6)
H13	0.1006	0.6786	0.5216	0.022*
C14	0.1986 (3)	0.74094 (8)	0.5832 (4)	0.0165 (6)
C15	0.3483 (3)	0.76498 (8)	0.6542 (3)	0.0162 (6)
H15	0.3440	0.7966	0.6610	0.019*
C16	0.5015 (3)	0.74254 (9)	0.7139 (4)	0.0176 (6)
H16	0.6040	0.7588	0.7617	0.021*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0193 (10)	0.0228 (11)	0.0302 (11)	0.0076 (8)	0.0082 (8)	0.0052 (9)
O2	0.0152 (9)	0.0201 (10)	0.0195 (10)	0.0065 (8)	0.0028 (7)	0.0045 (8)
O3	0.0188 (10)	0.0228 (11)	0.0200 (10)	0.0060 (8)	0.0070 (8)	0.0085 (8)
O4	0.0163 (9)	0.0172 (10)	0.0195 (10)	0.0054 (7)	0.0023 (7)	0.0049 (8)
O5	0.0257 (11)	0.0204 (12)	0.0337 (12)	0.0076 (9)	0.0015 (8)	0.0010 (9)
O6	0.0173 (10)	0.0360 (13)	0.0332 (12)	−0.0005 (9)	−0.0068 (9)	−0.0050 (10)
N1	0.0213 (12)	0.0170 (13)	0.0311 (13)	0.0035 (10)	−0.0030 (10)	−0.0009 (11)
N2	0.0183 (12)	0.0219 (14)	0.0178 (12)	0.0011 (10)	0.0028 (9)	−0.0001 (10)
C1	0.0207 (14)	0.0123 (14)	0.0201 (14)	0.0010 (12)	0.0005 (11)	0.0014 (11)
C2	0.0160 (13)	0.0131 (14)	0.0165 (13)	−0.0013 (10)	0.0012 (10)	−0.0016 (11)
C3	0.0133 (13)	0.0136 (14)	0.0189 (13)	0.0016 (11)	−0.0017 (10)	−0.0027 (11)
C4	0.0157 (13)	0.0139 (14)	0.0171 (13)	−0.0008 (10)	0.0015 (10)	−0.0010 (11)

C5	0.0154 (13)	0.0147 (14)	0.0174 (13)	−0.0017 (11)	0.0039 (10)	−0.0015 (11)
C6	0.0136 (13)	0.0142 (14)	0.0230 (14)	0.0022 (11)	−0.0003 (11)	0.0002 (11)
C7	0.0190 (14)	0.0098 (14)	0.0141 (13)	−0.0002 (10)	−0.0012 (10)	−0.0018 (11)
C8	0.0207 (14)	0.0211 (16)	0.0227 (14)	0.0046 (12)	−0.0017 (11)	0.0062 (12)
C9	0.0239 (15)	0.0173 (15)	0.0185 (14)	0.0015 (11)	0.0035 (11)	0.0044 (12)
C10	0.0148 (13)	0.0199 (15)	0.0230 (14)	0.0057 (11)	0.0004 (11)	0.0045 (12)
C11	0.0205 (14)	0.0186 (15)	0.0118 (13)	0.0037 (11)	0.0052 (11)	−0.0005 (11)
C12	0.0246 (14)	0.0121 (14)	0.0200 (14)	−0.0020 (12)	0.0025 (11)	0.0003 (11)
C13	0.0175 (14)	0.0218 (16)	0.0166 (14)	−0.0044 (12)	0.0029 (11)	−0.0013 (12)
C14	0.0154 (13)	0.0175 (15)	0.0168 (13)	0.0009 (11)	0.0011 (10)	0.0009 (11)
C15	0.0212 (14)	0.0122 (14)	0.0158 (13)	−0.0003 (11)	0.0056 (11)	−0.0014 (11)
C16	0.0165 (13)	0.0210 (16)	0.0152 (13)	0.0000 (11)	0.0011 (11)	−0.0023 (11)

Geometric parameters (Å, °)

O1—C1	1.229 (3)	C6—C7	1.374 (3)
O2—C3	1.357 (3)	C6—H6	0.9500
O2—C8	1.441 (3)	C8—H8A	0.9800
O3—C5	1.358 (3)	C8—H8B	0.9800
O3—C9	1.428 (3)	C8—H8C	0.9800
O4—C7	1.360 (3)	C9—H9A	0.9800
O4—C10	1.444 (3)	C9—H9B	0.9800
O5—N2	1.239 (3)	C9—H9C	0.9800
O6—N2	1.242 (3)	C10—H10A	0.9800
N1—C11	1.352 (3)	C10—H10B	0.9800
N1—H11	0.8600	C10—H10C	0.9800
N1—H12	0.8600	C11—C16	1.406 (4)
N2—C14	1.434 (3)	C11—C12	1.410 (3)
C1—C2	1.454 (3)	C12—C13	1.370 (3)
C1—H1	0.9500	C12—H12A	0.9500
C2—C3	1.409 (3)	C13—C14	1.393 (3)
C2—C7	1.424 (3)	C13—H13	0.9500
C3—C4	1.390 (3)	C14—C15	1.394 (3)
C4—C5	1.389 (3)	C15—C16	1.368 (3)
C4—H4	0.9500	C15—H15	0.9500
C5—C6	1.397 (3)	C16—H16	0.9500
C3—O2—C8	118.10 (19)	O2—C8—H8C	109.5
C5—O3—C9	118.39 (19)	H8A—C8—H8C	109.5
C7—O4—C10	117.03 (19)	H8B—C8—H8C	109.5
C11—N1—H11	120.0	O3—C9—H9A	109.5
C11—N1—H12	120.0	O3—C9—H9B	109.5
H11—N1—H12	120.0	H9A—C9—H9B	109.5
O5—N2—O6	121.4 (2)	O3—C9—H9C	109.5
O5—N2—C14	119.5 (2)	H9A—C9—H9C	109.5
O6—N2—C14	119.1 (2)	H9B—C9—H9C	109.5
O1—C1—C2	127.8 (2)	O4—C10—H10A	109.5
O1—C1—H1	116.1	O4—C10—H10B	109.5
C2—C1—H1	116.1	H10A—C10—H10B	109.5
C3—C2—C7	117.2 (2)	O4—C10—H10C	109.5

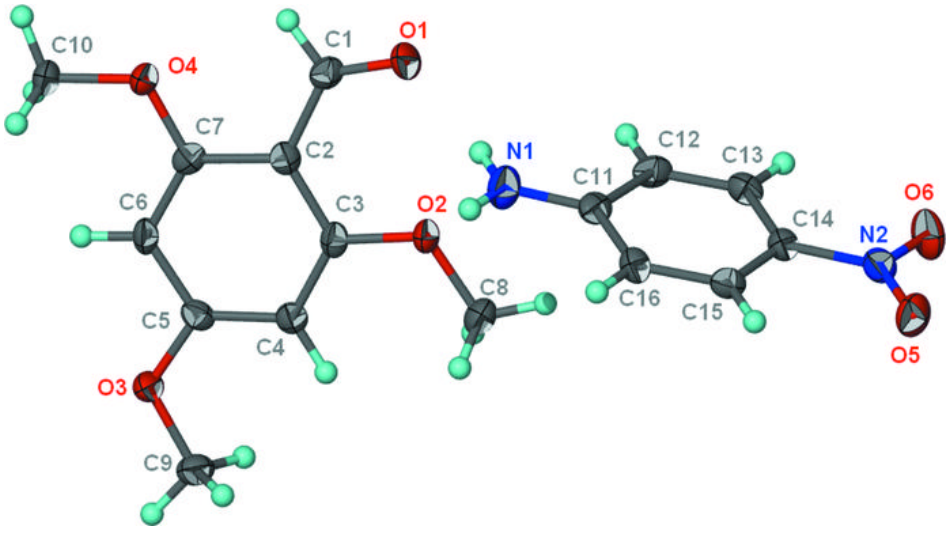
C3—C2—C1	124.5 (2)	H10A—C10—H10C	109.5
C7—C2—C1	118.3 (2)	H10B—C10—H10C	109.5
O2—C3—C4	122.4 (2)	N1—C11—C16	120.7 (2)
O2—C3—C2	115.5 (2)	N1—C11—C12	120.9 (2)
C4—C3—C2	122.1 (2)	C16—C11—C12	118.3 (2)
C3—C4—C5	118.2 (2)	C13—C12—C11	120.8 (2)
C3—C4—H4	120.9	C13—C12—H12A	119.6
C5—C4—H4	120.9	C11—C12—H12A	119.6
O3—C5—C4	123.9 (2)	C12—C13—C14	119.4 (2)
O3—C5—C6	114.1 (2)	C12—C13—H13	120.3
C4—C5—C6	122.0 (2)	C14—C13—H13	120.3
C7—C6—C5	119.0 (2)	C15—C14—C13	121.1 (2)
C7—C6—H6	120.5	C15—C14—N2	119.1 (2)
C5—C6—H6	120.5	C13—C14—N2	119.7 (2)
O4—C7—C6	123.1 (2)	C16—C15—C14	119.2 (2)
O4—C7—C2	115.4 (2)	C16—C15—H15	120.4
C6—C7—C2	121.5 (2)	C14—C15—H15	120.4
O2—C8—H8A	109.5	C15—C16—C11	121.2 (2)
O2—C8—H8B	109.5	C15—C16—H16	119.4
H8A—C8—H8B	109.5	C11—C16—H16	119.4
O1—C1—C2—C3	−9.3 (4)	C5—C6—C7—C2	−0.9 (4)
O1—C1—C2—C7	172.5 (2)	C3—C2—C7—O4	179.9 (2)
C8—O2—C3—C4	1.2 (3)	C1—C2—C7—O4	−1.8 (3)
C8—O2—C3—C2	−177.9 (2)	C3—C2—C7—C6	0.2 (3)
C7—C2—C3—O2	179.5 (2)	C1—C2—C7—C6	178.6 (2)
C1—C2—C3—O2	1.3 (4)	N1—C11—C12—C13	176.7 (2)
C7—C2—C3—C4	0.5 (3)	C16—C11—C12—C13	−2.2 (4)
C1—C2—C3—C4	−177.7 (2)	C11—C12—C13—C14	1.3 (4)
O2—C3—C4—C5	−179.5 (2)	C12—C13—C14—C15	0.2 (4)
C2—C3—C4—C5	−0.5 (4)	C12—C13—C14—N2	177.8 (2)
C9—O3—C5—C4	−0.4 (3)	O5—N2—C14—C15	−2.2 (3)
C9—O3—C5—C6	179.3 (2)	O6—N2—C14—C15	176.9 (2)
C3—C4—C5—O3	179.4 (2)	O5—N2—C14—C13	−179.9 (2)
C3—C4—C5—C6	−0.2 (4)	O6—N2—C14—C13	−0.8 (3)
O3—C5—C6—C7	−178.8 (2)	C13—C14—C15—C16	−0.6 (4)
C4—C5—C6—C7	0.9 (4)	N2—C14—C15—C16	−178.3 (2)
C10—O4—C7—C6	0.3 (3)	C14—C15—C16—C11	−0.3 (4)
C10—O4—C7—C2	−179.4 (2)	N1—C11—C16—C15	−177.2 (2)
C5—C6—C7—O4	179.5 (2)	C12—C11—C16—C15	1.7 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H12···O1	0.86	2.16	3.016 (3)	172
N1—H11···O5^{i}	0.86	2.50	3.288 (3)	152
N1—H11···O6^{i}	0.86	2.50	3.293 (3)	154

Symmetry codes: (i) *x*+1, −*y*+3/2, *z*+1/2.

Fig. 1


C10
O4
C1
O1
C7
C2
N1
C12
C13
C11
C6
C3
O2
C14
O6
N2
C8
C16
C15
C5
C4
O5
O3
C9