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

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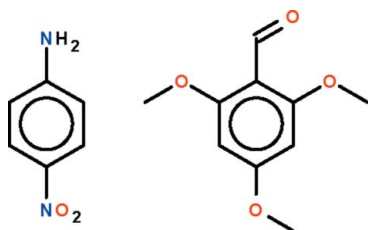
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 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.049; wR factor = 0.124; data-to-parameter ratio = 12.3.

In the title co-crystal, $\text{C}_6\text{H}_6\text{N}_2\text{O}_2 \cdot \text{C}_{10}\text{H}_{12}\text{O}_4$, the two components are held together by an $\text{N}-\text{H} \cdots \text{O}_{\text{aldehyde}}$ hydrogen bond. Adjacent co-crystals are linked by weaker $\text{N}-\text{H} \cdots \text{O}_{\text{nitro}}$ hydrogen bonds, forming a linear chain. The two aromatic rings of the components are aligned at $75.2(1)^\circ$. 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

 $\text{C}_6\text{H}_6\text{N}_2\text{O}_2 \cdot \text{C}_{10}\text{H}_{12}\text{O}_4$
 $M_r = 334.32$

 Monoclinic, $P2_1/c$
 $a = 7.4409(11)$ Å
 $b = 30.022(5)$ Å
 $c = 6.9400(11)$ Å
 $\beta = 93.237(3)^\circ$
 $V = 1547.9(4)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 100$ K
 $0.15 \times 0.10 \times 0.05$ mm

Data collection

 Bruker SMART APEX
 diffractometer
 8127 measured reflections

 2722 independent reflections
 1834 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$

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
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.41$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H12} \cdots \text{O1}$	0.86	2.16	3.016 (3)	172
$\text{N1}-\text{H11} \cdots \text{O5}^i$	0.86	2.50	3.288 (3)	152
$\text{N1}-\text{H11} \cdots \text{O6}^i$	0.86	2.50	3.293 (3)	154

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

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

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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-trimethoxybenzaldehyde 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 \cdots O hydrogen bond; the two aromatic rings aligned at 75.2 (1)°. Adjacent co-crystals are linked by weaker *N*–H \cdots 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; $U(\text{H})$ 1.2 to 1.5 $U_{\text{eq}}(\text{C},\text{N})$] 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

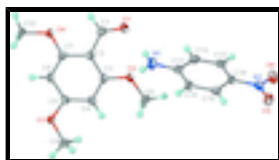


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of the C₆H₆N₂O₂–C₁₀H₁₂O₄ co-crystal at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

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

Crystal data

C₆H₆N₂O₂·C₁₀H₁₂O₄

$F(000) = 704$

supplementary materials

$M_r = 334.32$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.4409$ (11) Å

$b = 30.022$ (5) Å

$c = 6.9400$ (11) Å

$\beta = 93.237$ (3)°

$V = 1547.9$ (4) Å³

$Z = 4$

$D_x = 1.435$ Mg m⁻³

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

Cell parameters from 1019 reflections

$\theta = 2.7$ – 24.4 °

$\mu = 0.11$ mm⁻¹

$T = 100$ K

Prism, yellow

$0.15 \times 0.10 \times 0.05$ mm

Data collection

Bruker SMART APEX
diffractometer

Radiation source: fine-focus sealed tube
graphite

ω scans

8127 measured reflections

2722 independent reflections

1834 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.059$

$\theta_{\text{max}} = 25.0$ °, $\theta_{\text{min}} = 1.4$ °

$h = -8$ → 8

$k = -32$ → 35

$l = -8$ → 8

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.124$

$S = 1.01$

2722 reflections

221 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.141P]$

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

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

$\Delta\rho_{\text{max}} = 0.22$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.41$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^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)

supplementary materials

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 (\AA , $^\circ$)

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 (\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>
N1—H12 \cdots O1	0.86	2.16	3.016 (3)	172
N1—H11 \cdots O5 ⁱ	0.86	2.50	3.288 (3)	152
N1—H11 \cdots O6 ⁱ	0.86	2.50	3.293 (3)	154

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

Fig. 1

