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# Hydrogen bonding in *C*-methylated nitroanilines: three triclinic examples with *Z*′ = 2 or 4

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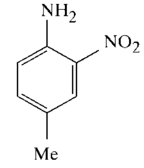
4-Methyl-2-nitroaniline, (I), $C_7H_8N_2O_2$, crystallizes with two molecules in the asymmetric unit. The molecules both form intramolecular N—H···O hydrogen bonds and they are linked into hydrogen-bonded $C_2^2(12)$ chains in which the two independent molecules alternate. 4,5-Dimethyl-2-nitroaniline, (II), $C_8H_{10}N_2O_2$, also has $Z' = 2$ and the two independent molecules each form hydrogen-bonded $C(6)$ chains. In 4-methyl-3-nitroaniline, (III), $C_7H_8N_2O_2$, there are four molecules in the asymmetric unit. Molecules of two of these types are linked by N—H···O hydrogen bonds into molecular ladders containing $R_4^3(18)$ rings and the other two types independently form single $C(7)$ chains.

## Comment

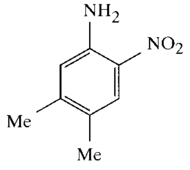
The three isomers of nitroaniline, $O_2NC_6H_4NH_2$, exhibit markedly different patterns of supramolecular aggregation. Thus, in the 1,4-isomer [Cambridge Structural Database (CSD; Allen & Kennard, 1993) refcode NANILI02; Tonogaki *et al.*, 1993], each molecule acts as a double donor and a double acceptor of N—H···O hydrogen bonds, and the molecules are thereby linked into (4,4) nets (Batten & Robson, 1998) in which the nodes are single molecules. The resulting sheets, built from a single type of $R_4^4(22)$ ring (Bernstein *et al.*, 1995), are weakly linked by aromatic $\pi$–$\pi$-stacking interactions.

Molecules of the 1,3-isomer (CSD refcode MNIANL01; Ploug-Sørensen & Andersen, 1986) also act as double donors and double acceptors, but now the molecules are linked by equal numbers of N—H···O and N—H···N hydrogen bonds, with only one of the nitro-O atoms involved. The molecules form (4,4) nets built from $R_4^4(18)$ rings, with no significant $\pi$–$\pi$-stacking interactions between neighbouring sheets.

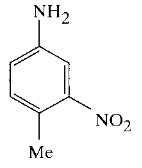
The 1,2-isomer (CSD refcode ONITAN; Dhaneshwar *et al.*, 1978) crystallizes in space group $P2_1/a$ with $Z' = 2$. Each of the independent molecules forms an intramolecular N—H···O hydrogen bond, generating an $S(6)$ motif, and the molecules are linked by further N—H···O hydrogen bonds into continuous $C_2^2(12)$ chains in which the two independent molecules alternate. These chains run parallel to the [011] direction in the domain $-0.34 < x < 0.34$ and parallel to $[01\bar{1}]$ in the domain $0.16 < x < 0.84$, so that the entire structure is a criss-cross stack, with chains in alternate layers inclined to one another by *ca* 81°. As in the 1,3-isomer, there are no $\pi$–$\pi$-stacking interactions between the chains.



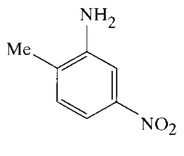
(I)



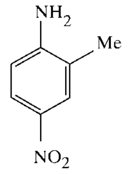
(II)



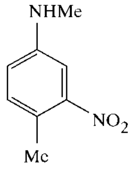
(III)



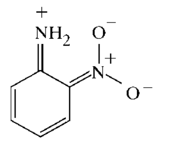
(IV)



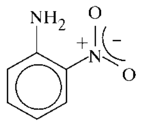
(V)



(VI)



(VII*a*)



(VII*b*)

In view of this wide disparity of structural types, it is of interest to investigate the supramolecular aggregation of *C*-methylated nitroanilines to determine the effects of substituents of modest steric bulk. We present here the structures of

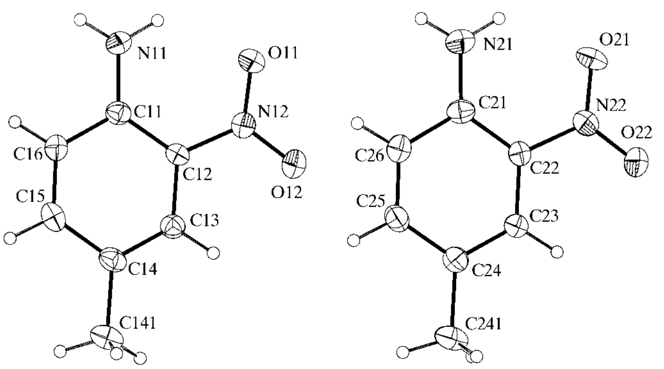


**Figure 1**
Views of the two independent molecules in (I) with the atom-labelling schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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three such *C*-methylated nitroanilines, namely 4-methyl-2-nitroaniline, (I), 4,5-dimethyl-2-nitroaniline, (II), and 4-methyl-3-nitroaniline, (III).

The crystals of (I) are triclinic, $P\bar{1}$, with $Z' = 2$. In each of the independent molecules (Fig. 1), there is an intramolecular N—H···O hydrogen bond forming an *S*(6) motif, and the molecules are linked into $C_2^2(12)$ chains running parallel to the [001] direction, in which molecules of the two types alternate (Fig. 2), as in ONITAN. However, the chain-forming hydrogen bonds (Table 2) differ from those in ONITAN. While N11 at ($x$, $y$, $z$) acts as donor, *via* H12, to O22$^{\rm i}$ [symmetry code: (i) $x$, $y$, $z - 1$], by contrast N21 acts as donor, *via* H22, to both O11 and O22 in an almost planar three-centre system, forming an $R_1^2(4)$ motif (Fig. 2). This asymmetric bifurcated type of hydrogen bond, although absent from the three isomers of nitroaniline, is, in fact, the commonest mode of hydrogen bonding to *C*-nitro groups (Allen *et al.*, 1997). In addition, C16 at ($x$, $y$, $z$) acts as donor to O21$^{\rm i}$, forming a rather weak C—H···O hydrogen bond and so completing an $R_2^2(8)$ motif. Thus, there are alternating $R_1^2(4)$ and $R_2^2(8)$ rings embedded in the $C_2^2(12)$ chain (Fig. 2). In compound (I), all the $C_2^2(12)$ chains are parallel with one another, in contrast with the criss-cross arrangement in ONITAN. Thus, (I) differs from its unsubstituted analogue, 2-nitroaniline, both in the form of the hydrogen bonding and in the stacking of the resulting chains; there are no $\pi$–$\pi$-stacking interactions in either compound. The CSD records a polymorph of (I) (CSD refcode TEHGUI; Ellena *et al.*, 1996) crystallized from acetone [*cf.* (I) crystallized from ethanol]. This second form is monoclinic, $C2/c$, with $Z = 8$. Each molecule forms an intramolecular N—H···O hydrogen bond in the usual *S*(6) motif, and they are linked by a single type of unbifurcated N—H···O hydrogen bond into zigzag *C*(6) chains along [001] generated by glide planes. These chains are weakly coupled into pairs by means of aromatic $\pi$–$\pi$-stacking interactions.

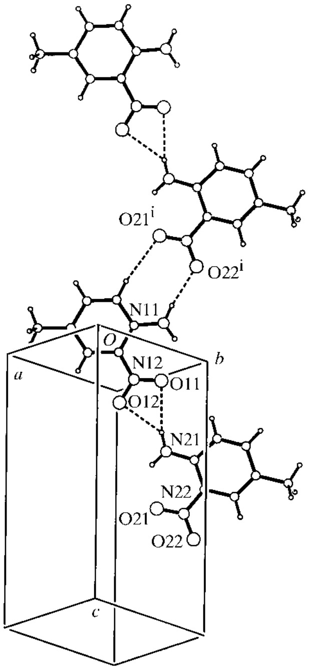

**Figure 2**
Part of the crystal structure of (I), showing the formation of a $C_2^2(12)$ chain parallel to [001] [symmetry code: (i) $x$, $y$, $z - 1$].

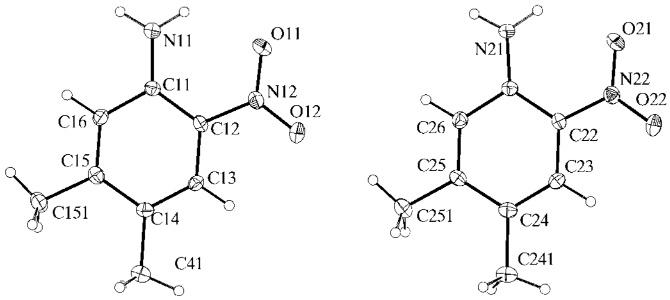

**Figure 3**
Views of the two independent molecules in (II) with the atom-labelling schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

The introduction of a second *C*-methyl group into 2-nitroaniline to give (II) generates a pattern of intermolecular aggregation different from that in (I). Each of the two independent molecules in (II) forms an intramolecular *S*(6) motif (Fig. 3) and each type of molecule separately forms *C*(6) chains built from N—H···O hydrogen bonds (Table 4). These chains are generated by translation and run parallel to [100] (Fig. 4). There is, in addition, a C—H···O hydrogen bond in one of the chains (Table 4) which reinforces the effect of the intermolecular N—H···O hydrogen bond by forming an $R_2^1(6)$ ring. The chains formed by the two independent molecules occupy different domains of $z$: that formed by molecule *A* (containing N11) lies in the domain $0.29 < z < 0.71$, with the chain lying approximately along the line ($x, \frac{1}{4}, \frac{1}{2}$), while that formed by molecule *B* (containing N21) lies in the domain $-0.21 < z < 0.21$, approximately along the line ($x, \frac{1}{4}, 0$). In addition, the chains of each type are weakly linked by

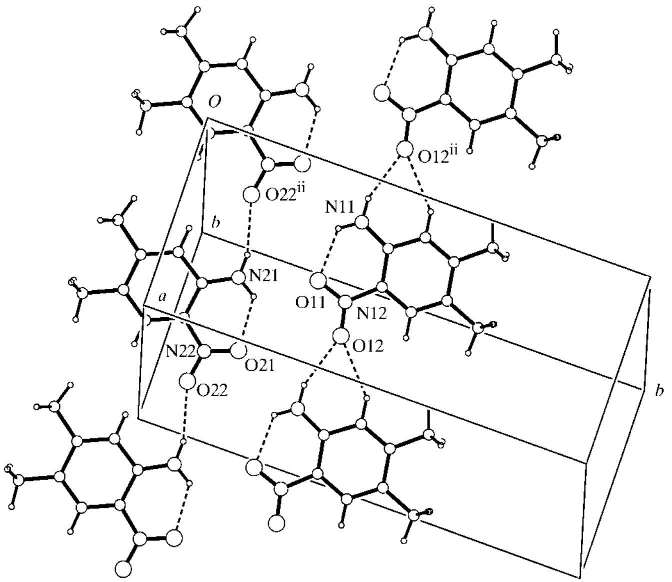

**Figure 4**
Part of the crystal structure of (II), showing the two independent chains parallel to [100] [symmetry code: (ii) $x - 1$, $y$, $z$].

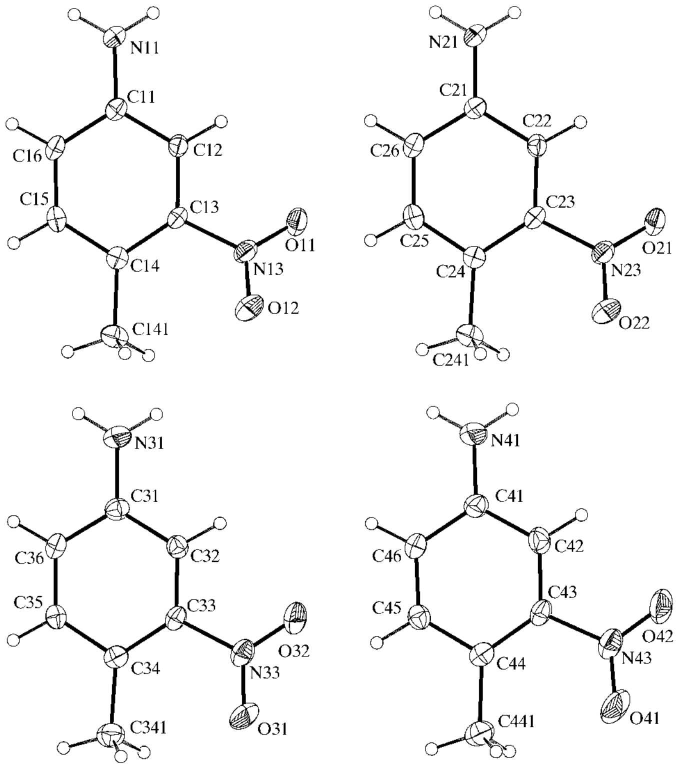

**Figure 5**
Views of the four independent molecules in (III) with the atom-labelling schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

aromatic π–π-stacking interactions. For molecules of type *A*, the ring at (*x*, *y*, *z*) forms π–π interactions with those at (−*x*, 1 − *y*, 1 − *z*) [interplanar spacing 3.448 (3) Å and centroid offset 1.442 (3) Å] and at (1 − *x*, −*y*, 1 − *z*) [interplanar spacing 3.407 (3) Å and centroid offset 1.739 (3) Å], so linking the neighbouring chains of *A*-type molecules into an (001) sheet. Similarly for molecules of type *B*, the ring at (*x*, *y*, *z*) is linked to those at (1 − *x*, 1 − *y*, −*z*) [interplanar spacing 3.405 (3) Å and centroid offset 1.323 (3) Å] and at (2 − *x*, −*y*, −*z*) [interplanar spacing 3.463 (3) Å and centroid offset 1.732 (3) Å], producing a similar sheet in the other domain of *z*. The overall 'millefeuille' structure thus consists of alternating sheets of *A* and *B* molecules, each comprising hydrogen-bonded chains linked by π–π-stacking interactions.

There are four independent molecules in 4-methyl-3-nitroaniline, (III) (Fig. 5), conveniently characterized as types *n* = 1–4, where type *n* contains atom N*n*1. Molecules of types 1, 2 and 3 act as single donors of N—H···O hydrogen bonds, and molecules of types 1, 3 and 4 act as single acceptors. Type 4 molecules are double donors and type 2 molecules are double acceptors (Table 6). Each type of molecule forms, by translation, a *C*(7) chain containing a single type of N—H···O hydrogen bond and running parallel to the [010] direction. There are thus eight chains passing through each unit cell. There are chains aligned approximately along (0.57, *y*, 0.31) and (0.07, *y*, 0.19) comprising molecules of types 1 and 2, respectively, in which the N—H···O hydrogen bonds are directed along the positive and negative directions of *b*, respectively (Table 6), and a similar pair containing molecules of types 3 and 4 aligned approximately along (0.17, *y*, 0.43) and (0.67, *y*, 0.07). In addition, there is a further set of four chains generated from the first set by the centres of inversion. The chains built of type 2 and type 4 molecules are linked in pairs by a further N—H···O hydrogen bond: N41 at (*x*, *y*, *z*) acts as donor, *via* H41*A*, to O21$^{\rm v}$ [symmetry refcode: (v) 1 − *x*, 1 − *y*, −*z*], while N41$^{\rm v}$ similarly acts as donor to O21 at (*x*, *y*, *z*). Hence, molecules of types 2 and 4 form a molecular ladder built of $R^3_4(18)$ rings (Fig. 6). The molecules of types 1 and 3, on the other hand, form isolated single chains of the type *C*(7). The CSD records a monoclinic polymorph of (III) (CSD refcode ZZZJIQ; Nigam & Murty, 1965), space group *A*2/*a* or *Aa*, whose cell dimensions are consistent with *Z* = 8. However, the atomic coordinates were not determined and the crystallization solvent was not recorded.

Compound (IV) (CSD refcode TIXQUM01; Ellena *et al.*, 1999) differs from (III) only in the location of its methyl group. Compound (IV) crystallizes in space group $P2_1/n$ with $Z' = 1$, and each molecule acts as a double donor and a double acceptor of N—H···O hydrogen bonds. The structure generated by these interactions comprises continuous sheets built from centrosymmetric $R^2_2(14)$ and $R^6_6(26)$ rings (Fig. 7) arranged in a chessboard fashion. The elegance and simplicity of this structure formed by N—H···O hydrogen bonds is unfortunately obscured in the original report by the inclusion

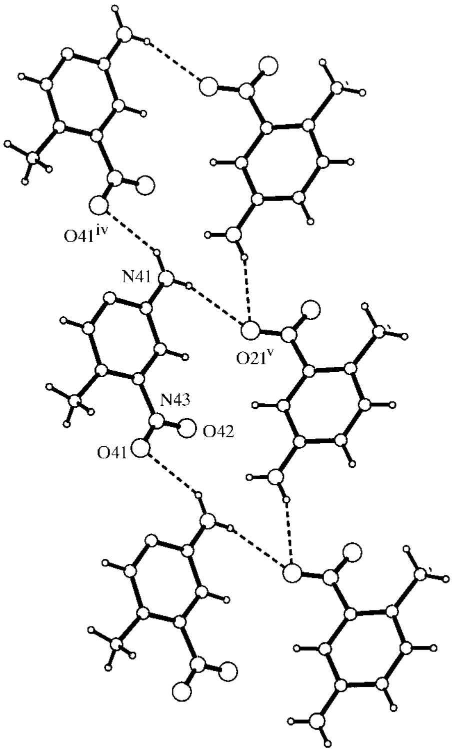

**Figure 6**
Part of the crystal structure of (III), showing the formation of a molecular ladder of $R^3_4(18)$ rings parallel to [010] and containing molecules of types 2 and 4. The unit-cell box is omitted for the sake of clarity [symmetry codes: (iv) *x*, *y* − 1, *z*; (v) 1 − *x*, 1 − *y*, −*z*].

of a large number of very weak C—H···O interactions, some of doubtful significance.

Compound (V) (CSD refcode BAJCIY; Lipscomb *et al.*, 1981) differs from (IV) only in the location of the nitro group. The crystals are monoclinic, space group *Cc*, but no atomic coordinates are recorded either in the original report or in the CSD.

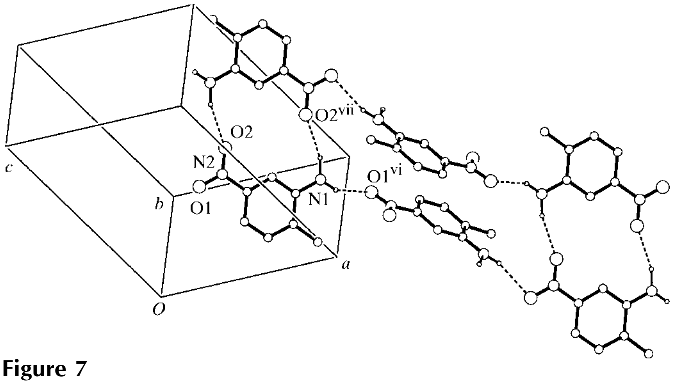

**Figure 7**
Part of the crystal structure of (IV), showing the formation of the $R_2^2(14)$ and $R_6^6(26)$ rings which generate the chessboard pattern. For the sake of clarity, H atoms bonded to carbon have been omitted [symmetry codes: (vi) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (vii) $2-x, 1-y, 1-z$].

Isomeric with (II) is the *N*-methyl compound (VI) (CSD refcode MNOMAN10; Chiaroni, 1971), in which the *N*-methyl group is *cisoid* to the nitro group. The molecules are linked by a single N—H···O hydrogen bond into *C*(7) chains generated by translation (Fig. 8).

In both (I) and (II), the C—C bond distances in the aryl rings (Tables 1 and 3) show marked quinonoid bond fixation, which is absent in (III). Moreover, both the C—NH$_2$ and C—NO$_2$ bond lengths in (I) and (II) are significantly shorter than the corresponding bonds in (III), whereas the N—O distances in (I) and (II) are significantly longer than those in (III) (Table 5). Thus, the canonical form (VII*a*) is a much more significant contributor in both (I) and (II) than in (III), which is itself better represented by (VII*b*).

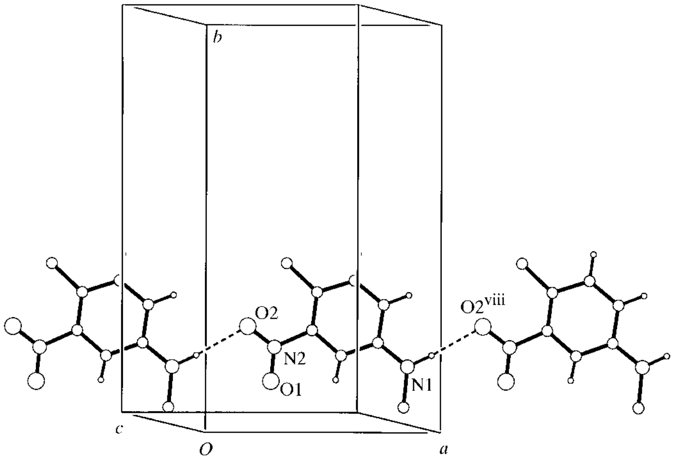

**Figure 8**
Part of the crystal structure of (VI) showing the formation of a *C*(7) chain [symmetry code: (viii) $1+x, y, z$].

## Experimental

Samples of compounds (I)–(III) were obtained from Aldrich. Crystals suitable for single-crystal X-ray diffraction were grown from solutions in ethanol.

### Compound (I)

*Crystal data*

| | |
|---|---|
| $C_7H_8N_2O_2$ | $Z = 4$ |
| $M_r = 152.15$ | $D_x = 1.422$ Mg m$^{-3}$ |
| Triclinic, $P\overline{1}$ | Mo $K\alpha$ radiation |
| $a = 7.8329$ (15) Å | Cell parameters from 11 810 reflections |
| $b = 7.990$ (2) Å | $\theta = 3.02$–$26.50°$ |
| $c = 12.369$ (3) Å | $\mu = 0.107$ mm$^{-1}$ |
| $\alpha = 79.766$ (17)° | $T = 150$ (2) K |
| $\beta = 81.257$ (19)° | Block, red |
| $\gamma = 69.646$ (8)° | 0.10 × 0.05 × 0.05 mm |
| $V = 710.8$ (3) Å$^3$ | |

*Data collection*

| | |
|---|---|
| KappaCCD diffractometer | 988 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans with $\kappa$ offsets | $R_{\rm int} = 0.014$ |
| Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997) | $\theta_{\rm max} = 26.5°$ |
| $T_{\rm min} = 0.989$, $T_{\rm max} = 0.995$ | $h = -9 \rightarrow 8$ |
| 22 499 measured reflections | $k = -8 \rightarrow 10$ |
| 2849 independent reflections | $l = -15 \rightarrow 13$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.071$ | $w = 1/[\sigma^2(F_o^2) + (0.0658P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.174$ | $(\Delta/\sigma)_{\rm max} = 0.016$ |
| $S = 0.833$ | $\Delta\rho_{\rm max} = 0.23$ e Å$^{-3}$ |
| 2849 reflections | $\Delta\rho_{\rm min} = -0.28$ e Å$^{-3}$ |
| 201 parameters | |

**Table 1**
Selected geometric parameters (Å) for (I).

| | | | |
|---|---|---|---|
| C11—C12 | 1.411 (5) | C21—C22 | 1.406 (5) |
| C12—C13 | 1.407 (5) | C22—C23 | 1.396 (5) |
| C13—C14 | 1.352 (5) | C23—C24 | 1.357 (5) |
| C14—C15 | 1.426 (5) | C24—C25 | 1.399 (5) |
| C15—C16 | 1.346 (5) | C25—C26 | 1.352 (5) |
| C16—C11 | 1.399 (5) | C26—C21 | 1.416 (5) |
| C11—N11 | 1.347 (4) | C21—N21 | 1.341 (5) |
| C12—N12 | 1.413 (4) | C22—N22 | 1.437 (5) |
| N12—O11 | 1.250 (4) | N22—O21 | 1.247 (4) |
| N12—O12 | 1.247 (4) | N22—O22 | 1.239 (4) |

**Table 2**
Hydrogen-bonding geometry (Å, °) for (I).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N11—H11···O11 | 0.88 | 1.99 | 2.625 (4) | 128 |
| N21—H21···O21 | 0.88 | 1.99 | 2.614 (4) | 127 |
| N11—H12···O22$^{i}$ | 0.88 | 2.14 | 2.987 (4) | 162 |
| N21—H22···O11 | 0.88 | 2.37 | 3.230 (4) | 165 |
| N21—H22···O12 | 0.88 | 2.41 | 3.105 (5) | 137 |
| C16—H16···O21$^{i}$ | 0.95 | 2.58 | 3.505 (5) | 164 |

Symmetry code: (i) $x, y, z-1$.

### Compound (II)

*Crystal data*

$C_8H_{10}N_2O_2$
$M_r = 166.18$
Triclinic, $P\overline{1}$
$a = 7.1422\ (14)$ Å
$b = 7.4564\ (15)$ Å
$c = 17.044\ (3)$ Å
$\alpha = 81.43\ (3)^\circ$
$\beta = 89.27\ (3)^\circ$
$\gamma = 61.84\ (3)^\circ$
$V = 789.6\ (3)$ Å$^3$

$Z = 4$
$D_x = 1.398$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3468 reflections
$\theta = 3.14$–$27.35^\circ$
$\mu = 0.103$ mm$^{-1}$
$T = 150\ (2)$ K
Plate, orange
$0.14 \times 0.12 \times 0.03$ mm

*Data collection*

KappaCCD diffractometer
$\varphi$ and $\omega$ scans with $\kappa$ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.986$, $T_{\max} = 0.997$
9952 measured reflections
3468 independent reflections

1988 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.060$
$\theta_{\max} = 27.35^\circ$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -21 \rightarrow 21$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.159$
$S = 0.958$
3468 reflections
221 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0797P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.28$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.37$ e Å$^{-3}$

**Table 3**
Selected geometric parameters (Å) for (II).

| | | | |
|---|---|---|---|
| C11—C12 | 1.407 (3) | C21—C22 | 1.411 (3) |
| C12—C13 | 1.401 (3) | C22—C23 | 1.403 (3) |
| C13—C14 | 1.367 (3) | C23—C24 | 1.368 (3) |
| C14—C15 | 1.419 (3) | C24—C25 | 1.417 (3) |
| C15—C16 | 1.371 (3) | C25—C26 | 1.367 (3) |
| C16—C11 | 1.408 (3) | C26—C21 | 1.409 (3) |
| C11—N11 | 1.344 (3) | C21—N21 | 1.345 (3) |
| C12—N12 | 1.433 (3) | C22—N22 | 1.420 (3) |
| N12—O11 | 1.246 (2) | N22—O21 | 1.243 (2) |
| N12—O12 | 1.237 (2) | N22—O22 | 1.241 (2) |

**Table 4**
Hydrogen-bonding geometry (Å, °) for (II).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N11—H11$\cdots$O11 | 0.88 | 2.02 | 2.638 (3) | 126 |
| N21—H21$\cdots$O21 | 0.88 | 2.03 | 2.642 (3) | 126 |
| N11—H12$\cdots$O12$^{\rm ii}$ | 0.88 | 2.29 | 3.102 (3) | 153 |
| N21—H22$\cdots$O22$^{\rm ii}$ | 0.88 | 2.26 | 3.078 (3) | 155 |
| C16—H16$\cdots$O12$^{\rm ii}$ | 0.95 | 2.52 | 3.325 (3) | 142 |

Symmetry code: (ii) $x - 1, y, z$.

### Compound (III)

*Crystal data*

$C_7H_8N_2O_2$
$M_r = 152.15$
Triclinic, $P\overline{1}$
$a = 7.3814\ (2)$ Å
$b = 8.2085\ (3)$ Å
$c = 23.5355\ (9)$ Å
$\alpha = 87.9310\ (13)^\circ$
$\beta = 89.8880\ (12)^\circ$
$\gamma = 88.371\ (2)^\circ$
$V = 1424.52\ (8)$ Å$^3$

$Z = 8$
$D_x = 1.419$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 5933 reflections
$\theta = 2.91$–$42.11^\circ$
$\mu = 0.107$ mm$^{-1}$
$T = 150\ (2)$ K
Plate, orange
$0.45 \times 0.20 \times 0.02$ mm

**Table 5**
Selected geometric parameters (Å) for (III).

| | | | |
|---|---|---|---|
| C11—N11 | 1.3782 (19) | C31—N31 | 1.380 (2) |
| C13—N13 | 1.4648 (18) | C33—N33 | 1.4657 (19) |
| N13—O11 | 1.2300 (17) | N33—O31 | 1.2134 (18) |
| N13—O12 | 1.2237 (17) | N33—O32 | 1.2177 (18) |
| C21—N21 | 1.3744 (19) | C41—N41 | 1.370 (2) |
| C23—N23 | 1.4682 (18) | C43—N43 | 1.469 (2) |
| N23—O21 | 1.2303 (17) | N43—O41 | 1.206 (2) |
| N23—O22 | 1.2246 (17) | N43—O42 | 1.2063 (19) |

*Data collection*

KappaCCD diffractometer
$\varphi$ and $\omega$ scans with $\kappa$ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.954$, $T_{\max} = 0.999$
14 564 measured reflections
6812 independent reflections

3517 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 27.5^\circ$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -30 \rightarrow 30$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.191$
$S = 0.969$
6812 reflections
401 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0972P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.33$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.38$ e Å$^{-3}$

**Table 6**
Hydrogen-bonding geometry (Å, °) for (III).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N11—H11$B\cdots$O11$^{\rm iii}$ | 0.88 | 2.38 | 3.236 (2) | 163 |
| N21—H21$B\cdots$O21$^{\rm iv}$ | 0.88 | 2.42 | 3.256 (2) | 158 |
| N31—H31$B\cdots$O31$^{\rm iii}$ | 0.88 | 2.31 | 3.099 (2) | 148 |
| N41—H41$B\cdots$O41$^{\rm iv}$ | 0.88 | 2.39 | 3.174 (2) | 149 |
| N41—H41$A\cdots$O21$^{\rm v}$ | 0.88 | 2.49 | 3.308 (2) | 154 |

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

Compounds (I)–(III) are all triclinic at 150 K; for each, the space group $P\overline{1}$ was assumed and confirmed by the analysis. H atoms were treated as riding, with C—H distances of 0.95 (aromatic) or 0.98 Å (methyl), and an N—H distance of 0.88 Å. For compound (I), it was evident that the methyl groups exhibited rotational disorder, and they were modelled using six half-occupancy sites, offset from one another by 60° rotations. Examination of the structures with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids.

For all compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1437). Services for accessing these data are described at the back of the journal.

## References

Allen, F. H., Baalham, C. A., Lommerse, J. P. M., Raithby, P. R. & Spark, E. (1997). *Acta Cryst.* B**53**, 1017–1024.

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 1460–1494.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.

Chiaroni, A. (1971). *Acta Cryst.* B**27**, 448–458.

Dhaneshwar, N. N., Tavale, S. S. & Pant, L. M. (1978). *Acta Cryst.* B**34**, 2507–2509.

Ellena, J., Goeta, A. E., Howard, J. A. K., Wilson, C. C., Autino, J. C. & Punte, G. (1999). *Acta Cryst.* B**55**, 209–215.

Ellena, J., Punte, G. & Rivero, B. E. (1996). *Acta Cryst.* C**52**, 2074–2076.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Lipscomb, G. F., Garito, A. F. & Narang, R. S. (1981). *Appl. Phys. Lett.* **38**, 663–665.

Nigam, G. D. & Murty, B. V. R. (1965). *Z. Kristallogr.* **122**, 318.

Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.

Ploug-Sørensen, G. & Andersen, E. K. (1986). *Acta Cryst.* C**42**, 1813–1815.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2000). *PLATON*. University of Utrecht, The Netherlands.

Tonogaki, M., Kawata, T., Ohba, S., Iwata, Y. & Shibuya, I. (1993). *Acta Cryst.* B**49**, 1031–1039.