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Stacking and N—H⋯O interactions in 2,3-dimethyl-6-nitroaniline

The non-H atoms of the title compound, $C_8H_{10}N_2O_2$, are almost coplanar. The conformation is stabilized by an intramolecular N—H⋯O hydrogen bond. The molecules are linked *via* intermolecular N—H⋯O hydrogen bonds into a one-dimensional chain. There are intermolecular C—H⋯π interactions and π⋯π stacking interactions present in the structure. The hydrogen-bonded chain is expanded into a three-dimensional net *via* stacking interactions.

Comment

In different nitroanilines, the supramolecular structures are mainly determined by intermolecular N—H⋯O hydrogen bonds (Garden *et al.*, 2002). Introducing other substituents, such as halogens, amines, carboxylic acids or even methyl groups, can, to a greater or lesser extent, influence the whole supramolecular assembly (Ploug-Sørensen & Andersen, 1986; Tonogaki *et al.*, 1993; Ellena *et al.*, 1999; Cannon *et al.*, 2001; Ferguson *et al.*, 2001). For example, in iodonitroanilines, the iodo–nitro interactions are substantial in supramolecular aggregation (Garden *et al.*, 2002), as was also found for iodobenzenoid compounds (Allen *et al.*, 1994; Thalladi *et al.*, 1996; Masciocchi *et al.*, 1998; Ranganathan & Pedireddi, 1998; McWilliam *et al.*, 2001). In these compounds, the hydrogen bonds mainly determine the two-dimensional supramolecular structure; the third dimension is achieved mainly by aromatic π–π stacking interactions (Hunter & Sanders, 1990). Although the supramolecular structures of compounds containing strong electron donor/acceptor substituents have been studied widely (Rychlewska & Warżajtis, 2001; Kelly *et al.*, 2002; Glidewell *et al.*, 2002, 2004), there have been only a small number of reports on the influence of methyl-substituted aromatic rings on the supramolecular structure. Thus, the synthesis and structural investigation of the title compound, (I), was undertaken.
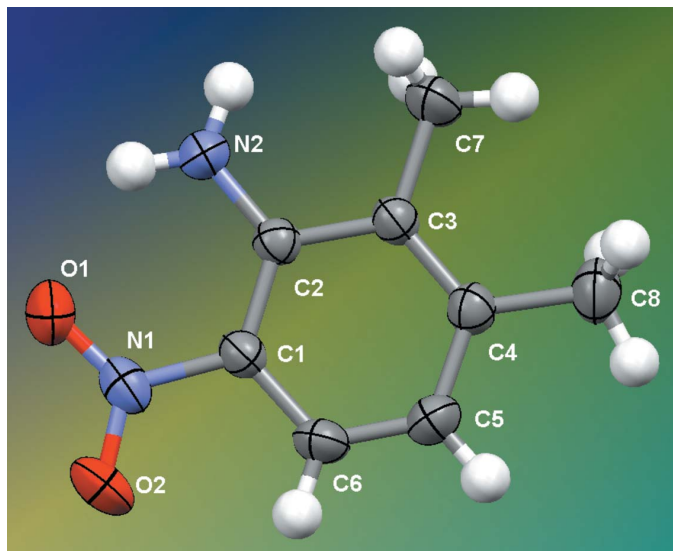

(I)
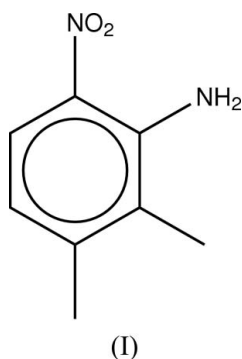
Figure 1
Molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

Figure 2
Part of the molecular packing of the title compound, showing inter-molecular N—H···O hydrogen bonds as dashed lines.

Compound (I) is a very compact molecule, possessing the following parts, which can participate in intermolecular interactions: nitro group, amine group, methyl groups, π system.

A perspective view of (I), together with the atom-numbering scheme, is shown in Fig. 1. All bond distances are normal. Atoms N1, N2, C7 and C8 deviate, respectively, by -0.044 (2), -0.036 (2), 0.034 (3) and -0.050 (3) Å from the least-squares plane of the benzene ring. The weighted least-squares plane through the atoms of the nitro group makes an angle of 2.30 (15)° with the above plane. This configuration is the result of an N—H···O intramolecular hydrogen bond (Taylor & Kennard, 1982; Desiraju & Steiner, 1999) (Table 1). The molecules of (I) are linked *via* intermolecular N—H···O hydrogen bonds into a one-dimensional chain along the crystallographic *c* axis. Furthermore, two additional short contacts can be found: C8—H8A···π^{ii} [π is the centre of the aromatic ring; symmetry code: (ii) $-x + 1$, $-y + 1$, $-z$; D···π = 3.612 (2) Å, H···π = 2.76 Å and D—H···π = 148°], π···π^{ii} and π···π^{iii} stacking interactions [symmetry code: (iii) $-x + \frac{1}{2}$, $-y + \frac{3}{2}$, $-z$; ring centroid distances 4.845 (2) and 3.733 (2) Å, perpendicular distances between symmetry-related parallel rings 3.530 (2) and 3.467 (2) Å, and angles between the vector linking ring centroids and the normal to one of the planes 43.2 (2) and 21.7 (2)°, respectively]. *Via* π···π stacking inter-actions, the hydrogen-bonded chain is expanded to form a three-dimensional net.

Experimental

The title compound was prepared according to the method of Noelting *et al.* (1901). The product was recrystallized from methanol, ethanol, acetonitrile, cyclohexane, ethylacetate and their mixtures (from equivolume amounts to five-times excess of one or more solvents). In all cases, similar prismatic crystals of (I) were obtained. The analytical data were in good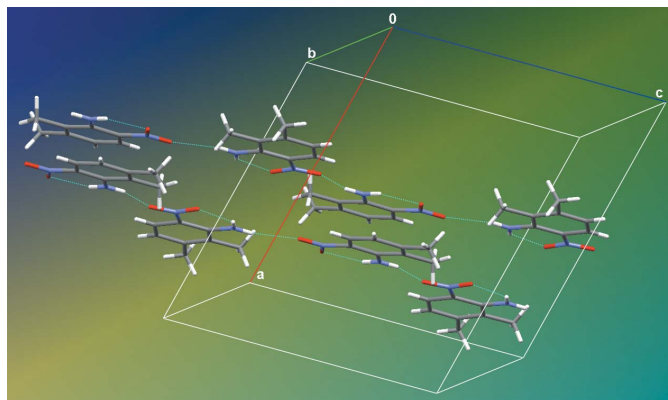 agreement with those reported in the literature (Courtin & von Tobel, 1980; Olah *et al.*, 1976; Divekar & Vining, 1964).

Crystal data

$C_8H_{10}N_2O_2$	$D_x = 1.349$ Mg m^{-3}
$M_r = 166.18$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 5030
$a = 14.4439$ (11) Å	reflections
$b = 8.6837$ (6) Å	$\theta = 2$–25°
$c = 14.0031$ (10) Å	$\mu = 0.10$ mm^{-1}
$\beta = 111.251$ (9)°	$T = 291.0$ (3) K
$V = 1636.9$ (2) Å^3	Prism, orange
$Z = 8$	$0.48 \times 0.40 \times 0.25$ mm

Data collection

Kuma KM-4 CCD diffractometer	1297 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.035$
Absorption correction: numerical	$\theta_{max} = 25.3$°
(X-RED; Stoe & Cie, 1999)	$h = -17 \rightarrow 17$
$T_{min} = 0.941$, $T_{max} = 0.991$	$k = -10 \rightarrow 10$
9090 measured reflections	$l = -16 \rightarrow 15$
1492 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0975P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.054$	$+ 0.2133P]$
$wR(F^2) = 0.163$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.17$	$(\Delta/\sigma)_{max} < 0.001$
1492 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
112 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1	0.87	2.02	2.654 (2)	128
N2—H2B···O2^i	0.87	2.25	3.035 (2)	150
C6—H6···O2	0.93	2.34	2.665 (2)	100

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

All C-bonded H atoms were placed in calculated positions and were refined as riding on their parent C atom [C—H = 0.93 (aromatic) and 0.96 Å (methyl), and U_{iso}(H) = 1.2U_{eq}(C$_{arom}$) and

$1.5U_{eq}(C_{methyl})]$. The methyl groups were allowed to rotate about their local threefold axis. The N-bonded H atoms were found in a difference Fourier synthesis and were refined as riding on their parent N atom $[U_{iso}(H) = 1.2U_{eq}(N)]$.

Data collection: *CrysAlisCCD* (UNIL IC & Kuma, 2000); cell refinement: *CrysAlisRED* (UNIL IC & Kuma, 2000); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Version 1.4; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

References

Allen, F. H., Goud, B. S., Hoy, V. J., Howard, J. A. K. & Desiraju, G. R. (1994). *J. Chem. Soc. Chem. Commun.* pp. 2729–2730.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M. K., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Cannon, D., Glidewell, C., Low, J. N., Quesada, A. & Wardell, J. L. (2001). *Acta Cryst.* C**57**, 216–221.
Courtin, A. & von Tobel, H.-R. (1980). *Helv. Chim. Acta*, **63**, 385–394.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford University Press.
Divekar, P. V. & Vining, L. C. (1964). *Can. J. Chem.* **42**, 63–68.
Ellena, J., Goeta, A. E., Howard, J. A. K., Wilson, C. C., Autino, J. C. & Punte, G. (1999). *Acta Cryst.* B**55**, 209–215.
Ferguson, G., Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2001). *Acta Cryst.* C**57**, 315–316.
Garden, S. J., Fontes, S. P., Wardell, J. L., Skakle, J. M. S., Low, J. N. & Glidewell, C. (2002). *Acta Cryst.* B**58**, 701–709.
Glidewell, C., Howie, R. A., Low, J. N., Skakle, J. M. S., Wardell, S. M. S. V. & Wardell, J. L. (2002). *Acta Cryst.* B**58**, 864–876.
Glidewell, C., Low, J. N., Skakle, J. M. S., Wardell, S. M. S. V. & Wardell J. L. (2004). *Acta Cryst.* B**60**, 472–480.
Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
Kelly, C. J., Skakle, J. M. S., Wardell, J. L., Wardell, S. M. S. V., Low, J. N. & Glidewell, C. (2002). *Acta Cryst.* B**58**, 94–108.
McWilliam, S. A., Skakle, J. M. S., Low, J. N., Wardell, J. L., Garden, S. J., Pinto, A. C., Torres, J. C. & Glidewell, C. (2001). *Acta Cryst.* C**57**, 942–945.
Masciocchi, N., Bergamo, M. & Sironi, A. (1998). *Chem. Commun.* pp. 1347–1348.
Noelting, E., Braun, A. & Thesmar, G. (1901). *Chem. Ber.* **34**, 2242–2262.
Olah, G. A., Lin, H. C. & Serianz, A. (1976). *Synthesis*, pp. 42–43.
Ploug-Sørensen, G. & Andersen, E. K. (1986). *Acta Cryst.* C**42**, 1813–1815.
Ranganathan, A. & Pedireddi, V. R. (1998). *Tetrahedron Lett.* **39**, 1803–1806.
Rychlewska, U. & Warżajtis, B. (2001). *Acta Cryst.* B**57**, 415–427.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Stoe & Cie (1999). *X-RED*. Version 1.18. Stoe & Cie GmbH, Darmstadt, Germany.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
Thalladi, V. R., Goud, S., Hoy, V. J., Allen, F. H., Howard, J. A. K. & Desiraju, G. R. (1996). *Chem. Commun.* pp. 401–402.
Tonogaki, M., Kawata, T., Ohba, S., Iwata, Y. & Shibuya, I. (1993). *Acta Cryst.* B**49**, 1031–1039.
UNIL IC & Kuma (2000). *CrysAlisCCD* and *CrysAlisRED*. Version 1.163. Kuma Diffraction Instruments GmbH, Wrocław, Poland.