Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Three-dimensional aggregation in 2-hydroxy-3-iodo-5-nitrobenzaldehyde involving C—H···O, iodo–nitro and aromatic π–π stacking interactions, and isolated dimers in disordered 2,4-diiodo-6-nitroanisole

Simon J. Garden,[a] Fernando R. da Cunha,[a] Christopher Glidewell,[b]* John N. Low,[c] Janet M. S. Skakle[c] and James L. Wardell[a]

[a]Departamento de Química Orgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil, [b]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland, and [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

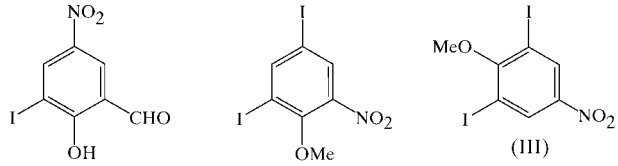
Received 3 November 2003
Accepted 6 November 2003
Online 6 December 2003

In 2-hydroxy-3-iodo-5-nitrobenzaldehyde, $C_7H_4INO_4$, the molecules are linked into sheets by a combination of C—H···O hydrogen bonds and two-centre iodo–nitro interactions, and these sheets are linked by aromatic π–π stacking interactions. Molecules of 2,4-diiodo-6-nitroanisole, $C_7H_5I_2NO_3$, are disordered, with the nitro group and one of the I substituents each occupying common sets of sites with 0.5 occupancy. The molecules are linked into isolated centrosymmetric dimeric units by a single iodo–nitro interaction.

Comment

We have recently reported the supramolecular aggregation of a wide range of different types of iodo–nitro aromatic compounds (McWilliam *et al.*, 2001; Garden, da Cunha *et al.*, 2002; Garden, Fontes *et al.*, 2002; Kelly *et al.*, 2002; Glidewell, Howie *et al.*, 2002; Glidewell, Low *et al.*, 2002; Glidewell *et al.*, 2003), in which the patterns of supramolecular aggregation depend on the interplay of a wide range of weak intermolecular forces, including hard and soft (Desiraju & Steiner, 1999) hydrogen bonds of various types, iodo–nitro interactions and aromatic π–π stacking interactions. We report here the molecular and supramolecular structures of two further examples of such compounds, *viz.* 2-hydroxy-3-iodo-5-nitrobenzaldehyde, (I), and 2,4-diiodo-6-nitroanisole, (II), the latter being isomeric with 2,6-diiodo-4-nitroanisole, (III) (Garden, da Cunha *et al.*, 2002).

In compound (I) [Fig. 1, where the crystallographic atom-numbering scheme differs from the conventional chemical



numbering scheme in order that both (I) and (II) have a nitro group at position 1 and an iodo substituent at position 5], there is an intramolecular O—H···O hydrogen bond, forming an *S*(6) motif (Bernstein *et al.*, 1995). There are three distinct types of intermolecular interactions linking the molecules of (I). A soft hydrogen bond and an iodo–nitro interaction each form a chain motif. Thus, aromatic atom C6 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor to the aldehydic atom O31 in the molecule at (1 + *x*, *y*, *z*), so generating by translation a *C*(7) chain running parallel to the [100] direction

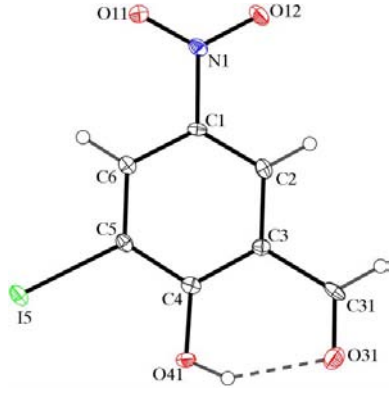


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

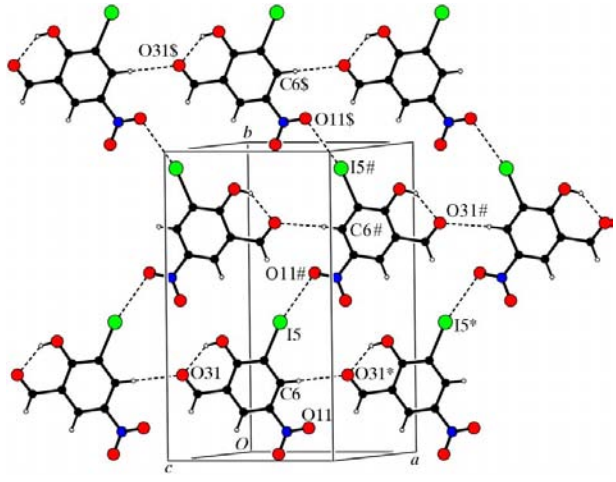


Figure 2
Part of the crystal structure of (I), showing the formation of an (001) sheet built from C—H···O hydrogen bonds and iodo–nitro interactions. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions (1 + *x*, *y*, *z*), (1 − *x*, $\frac{1}{2}$ + *y*, $\frac{1}{2}$ − *z*) and (*x*, 1 + *y*, *z*), respectively.

  DOI: 10.1107/S0108270103025654

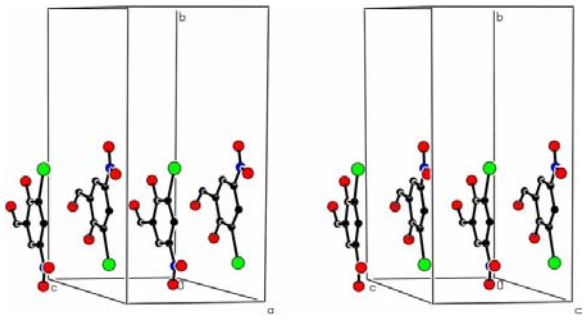


Figure 3
A stereoview of part of the crystal structure of (I), showing the π–π stacking interaction which links adjacent (001) sheets. For the sake of clarity, H atoms have been omitted.

(Fig. 2). At the same time, atom I5 in the molecule at (x, y, z) forms a short two-centre iodo–nitro interaction with nitro atom O11 in the molecule at $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, with I···O = 3.054 (3) Å, C—I···O = 167.8 (2)° and I···O—N = 116.0 (2)°, so producing a $C(6)$ chain (Starbuck *et al.*, 1999) running parallel to the [010] direction and generated by the 2_1 screw

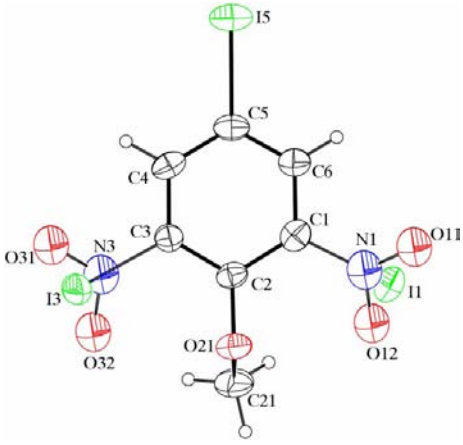


Figure 4
A view of the molecule of (II), showing the atom-labelling scheme and the disorder (see text). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

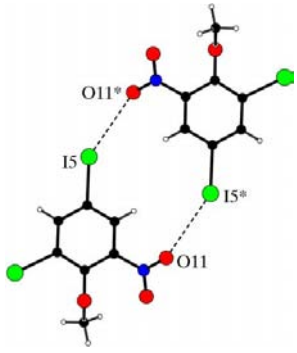


Figure 5
Part of the crystal structure of (II), showing the formation of an $R_2^2(14)$ dimer. For the sake of clarity, only one orientation of the disordered components is shown, and the H atoms and the unit-cell box have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$.

axis along $(\frac{1}{2}, y, \frac{1}{4})$. The combination of the [100] and [010] chains generates an elegant sheet parallel to (001) in the form of a (4,4)-net (Batten & Robson, 1998) containing equal numbers of $S(6)$ and $R_5^4(22)$ rings (Fig. 2).

Two sheets of this type pass through each unit cell of (I), lying in the domains $0.09 < z < 0.41$ and $0.59 < z < 0.91$, and adjacent sheets are weakly linked by the third type of intermolecular interaction, an aromatic π–π stacking interaction. The aryl ring in the molecule at (x, y, z), which lies in the $0.09 < z < 0.41$ sheet, and those in the molecules at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(x, \frac{1}{2} - y, z - \frac{1}{2})$, which lie in the domains $0.59 < z < 0.91$ and $-0.41 < z < -0.09$, respectively, are nearly parallel, with an interplanar angle between rings in adjacent sheets of only *ca* 1.3°. The centroid separations are both 3.767 (3) Å and the interplanar separations are *ca* 3.46 Å, corresponding to centroid offsets of *ca* 1.49 Å (Fig. 3).

In the disordered structure of (II) (Fig. 4, where again the crystallographic atom-numbering scheme differs from the conventional chemical numbering scheme, see above), in contrast with (I), there are neither C—H···O hydrogen bonds nor aromatic π–π stacking interactions. The only direction-specific intermolecular interaction is a two-centre iodo–nitro interaction involving the fully occupied I5 site and the half-occupied O1 site in the molecules at (x, y, z) and $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$, with I···O = 3.339 (13) Å, C—I···O = 148.5 (2)° and I···O—N = 135.3 (13)°. If the O11 sites in both of these molecules were fully occupied, the resulting dimer would contain an $R_2^2(14)$ motif (Fig. 5). However, each such pair of molecules may, in fact, contain two, one or zero I···O interactions, depending upon the local occupancy of the O11 sites, with an average value of one. There are four of these dimeric aggregates in each unit cell of (II), but there are no direction-specific interactions between them. In the isomeric compound, (III), the fully ordered molecules are linked into isolated chains by a single two-centre iodo–nitro interaction (Garden, da Cunha *et al.*, 2002). The intramolecular distances and angles in (I) and (II) present no unusual features.

Experimental

To prepare compound (I), 5-nitrosalicylaldehyde (10 mmol) was dissolved in warm methanol (30 ml) and a solution of $K[ICl_2]$ in methanol (2 *M*, 10 ml) was added with stirring. After a few hours, the reaction mixture was diluted with water (100 ml) and compound (I) was collected by filtration, washed with water and crystallized from aqueous ethanol (yield 83%, m.p. 432–433 K). To prepare compound (II), a solution of $K[ICl_2]$ in methanol (2 *M*, 25 ml) was added to a methanol solution (50 ml) of 2-nitrophenol (20 mmol) and the mixture was gently warmed. Water (100 ml) was added to the reaction mixture and the 2,4-diiodo-6-nitrophenol which precipitated out was collected by filtration and washed with water. This material was dissolved in acetone (50 ml) and to this solution was added K_2CO_3 (30 mmol) followed by an excess of Me_2SO_4 (10 ml). The resulting mixture was stirred at room temperature for 3 d, after which time the reaction mixture was concentrated by evaporation of the volatiles. The addition of water (100 ml) prompted the precipitation of compound (II), which was collected by filtration and crystallized from aqueous ethanol (yield 93%, m.p. 385–386 K).

Compound (I)

Crystal data

$C_7H_4INO_4$
M_r = 293.01
Monoclinic, $P2_1/c$
a = 8.2556 (3) Å
b = 15.3414 (8) Å
c = 7.2521 (4) Å
β = 115.496 (3)°
V = 829.05 (7) Å^3
Z = 4
D_x = 2.348 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1901 reflections
θ = 3.0–27.5°
μ = 3.84 mm^{-1}
T = 120 (2) K
Lath, colourless
0.36 × 0.05 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.339, T_{max} = 0.927
8251 measured reflections
1901 independent reflections
1482 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 27.5°
$h = -10 \rightarrow 10$
$k = -19 \rightarrow 19$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.074
S = 1.03
1901 reflections
119 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.13 e Å^{-3}
$\Delta\rho_{min}$ = −1.08 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O41—H41···O31	0.82	1.92	2.629 (5)	145
C6—H6···O31^{i}	0.93	2.48	3.351 (6)	155

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

Compound (II)

Crystal data

$C_7H_5I_2NO_3$
M_r = 404.92
Monoclinic, $C2/c$
a = 32.999 (2) Å
b = 4.2305 (3) Å
c = 14.8328 (11) Å
β = 95.225 (2)°
V = 2062.1 (2) Å^3
Z = 8
D_x = 2.609 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3712 reflections
θ = 2.5–32.6°
μ = 6.08 mm^{-1}
T = 120 (2) K
Needle, colourless
0.34 × 0.04 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.232, T_{max} = 0.793
10 606 measured reflections
3712 independent reflections
1520 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 32.6°
$h = -49 \rightarrow 33$
$k = -6 \rightarrow 6$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.154
S = 0.89
3712 reflections
126 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0721P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.07 e Å^{-3}
$\Delta\rho_{min}$ = −1.29 e Å^{-3}

The crystals of (I) and (II) are monoclinic. For (I), the space group $P2_1/c$ was uniquely assigned from the systematic absences, while for (II), the systematic absences permitted Cc and $C2/c$ as possible space groups; $C2/c$ was selected, and confirmed by the subsequent structure analysis. It was apparent at an early stage that the molecules of (II) were disordered over two sets of sites such that all atoms except one nitro group and one I atom were common to both orientations. When the site-occupancy factors for these disordered substituents were refined they gave values of 0.48 (3) and 0.52 (3), and hence they were both thereafter fixed at 0.50. When full anisotropic refinement was attempted for (II), the behaviour of the disordered nitro groups was erratic and not satisfactory. Accordingly, the atoms in these substituents were constrained to have the same anisotropic displacement parameters and the refinement then behaved satisfactorily. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.93 (aromatic and CHO) and 0.96 Å (methyl), and O—H distances of 0.82 Å.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1198). Services for accessing these data are described at the back of the journal.

References

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, pp. 86–89. Oxford University Press.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Garden, S. J., da Cunha, F. R., Wardell, J. L., Skakle, J. M. S., Low, J. N. & Glidewell, C. (2002). *Acta Cryst.* C**58**, o463–o466.
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, J. L. (2003). *Acta Cryst.* C**59**, o95–o97.
Glidewell, C., Low, J. N., Skakle, J. M. S., Wardell, S. M. S. V. & Wardell, J. L. (2002). *Acta Cryst.* C**58**, o487–o490.
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.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Starbuck, J., Norman, N. C. & Orpen, A. G. (1999). *New J. Chem.* **23**, 969–972.