Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(n-Nitrophenyl)acetonitrile, with n = 2, 3 and 4

Stepan Boitsov, Jon Songstad and Karl W. Törnroos*

Department of Chemistry, University of Bergen, Allégaten 41, 5007 Bergen, Norway
Correspondence e-mail: karl.tornroos@kj.uib.no

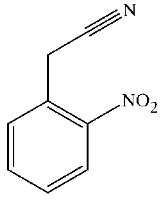
Received 5 June 2002
Accepted 28 June 2002
Online 31 July 2002

The molecular structures of the three title nitro-substituted phenylacetonitriles, $C_8H_6N_2O_2$, at 123 K show that the molecules are linked together very differently. In the 2- and 4-nitro compounds, there are both O$\cdots$H and $N_{cyano}\cdots H$ interactions, whereas the crystal lattice of the 3-nitro compound is essentially built up by O$\cdots$H interactions. The O atoms seem to prefer the aromatic H atoms, while the cyano N atoms prefer the methylene H atoms. The phenyl–nitro torsion angles are −19.83 (13), −5.69 (12) and −2.88 (12)°, while the phenyl–cyanomethyl torsion angles are −62.27 (12), −147.99 (9) and −16.75 (14)° in the 2-, 3- and 4-NO_2-substituted compounds, respectively.

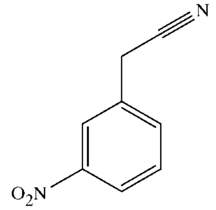
Comment

In recent years, the concept of weak and even very weak hydrogen bonds has been extensively used to rationalize crystal growth, molecular recognition and solvation phenomena (Desiraju & Steiner, 1999). According to this extended definition, hydrogen-bond distances between donor (D) and acceptor (A) atoms comparable to the sum of the van der Waals radii, and even slightly larger distances, have to be taken into account. The strength of an X—H$\cdots$$Y$ interaction undoubtedly increases the closer the bond angle at the H atom is to 180°, but it is now also suggested that significantly smaller angles may not exclude H$\cdots$$Y$ interactions (Thalladi *et al.*, 1998). Additionally, one has to consider other types of $D\cdots A$ interactions between functional groups, interactions which, in organic chemistry, are often termed through-space interactions or nucleophilic–electrophilic interactions (Schweizer *et al.*, 1978). These may have a dominating effect on crystal growth, in addition to their stereochemical control of many reactions (Nishide *et al.*, 2001). Since a crystal can, in principle, be considered as a supermolecule (Dunitz, 1991; Lehn, 1995), a more detailed analysis of all potential forces between molecules in crystals may lead to an improved knowledge of supermolecules and their formation.

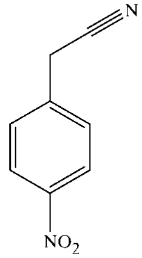
Fundamentally, one may assume that a crystallization process will be initiated by a close approach of the atoms forming the stronger contacts, in such a way that the repulsive interactions and steric demands of adjacent atoms are minimized, particularly when crystals are formed from very weakly solvating solvents (Shimon *et al.*, 1990). The order of the subsequent weaker interactions forming the crystal lattice may then be a consequence of the configurational and conformational demands set by the first interaction (Seiler & Dunitz, 1989). Thus, even for crystal lattices constructed through only weak interactions, one has to look for the strongest of the weak, *i.e.* whether certain combinations of D and A atoms are favoured over others. Here, we report the crystal structures of 2-, 3- and 4-nitrophenylacetonitrile, *viz.* (I), (II) and (III), respectively, which are well suited to this kind of study, since several types of interactions are possible in principle, allowing a comparison to be made.



(I)



(II)



(III)

The structure of (III) has been reported previously [Cambridge Structural Database (Allen & Kennard, 1993) refcode WIQDIJ] as part of a larger methodical study of structure solution and Rietveld refinement of powder diffraction data on organic substances that are difficult to crystallize (Goubitz *et al.*, 1999). The rather high melting points of the three compounds, characteristic for most nitro-substituted aromatic compounds, do indicate some strong intermolecular interactions or numerous weak ones. For these compounds, the following interactions should be considered, all of which have been repeatedly documented [the sums of the relevant van der Waals radii (Bondi, 1964) are given in parentheses]: N(CN)$\cdots$H(CH_2) and N(CN)$\cdots$H(Ar) (2.75 Å), O(NO_2)$\cdots$H(CH_2) and O(NO_2)$\cdots$H(Ar) (2.72 Å), O(NO_2)$\cdots$C(CN) and N(CN)$\cdots$C(CN) (3.22 and 3.25 Å, respectively), N(NO_2)$\cdots$O(NO_2), including four-membered cyclic systems (3.07 Å), and π–π stacking, H(CH_2)$\cdots\pi$ and H(Ar)$\cdots\pi$ interactions. Furthermore, different cyclic systems

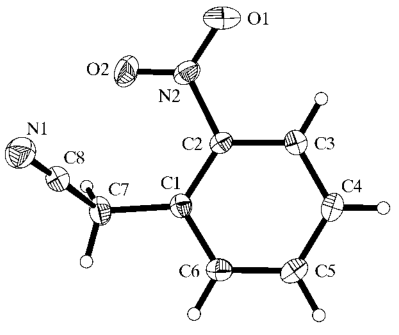


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

DOI: 10.1107/S0108270102011514

based upon the various interactions mentioned above should also be considered, *e.g.* cyclic dimers made by O(NO_2)···*ortho*-H(Ar) interactions (Jaiboon *et al.*, 2001).

For (2-nitrophenyl)acetonitrile, (I), all the intramolecular bond lengths and angles are as expected for this class of compounds (Higashi & Osaki, 1977; Di Rienzo *et al.*, 1980), only the bond between the C atoms bearing the substituents, C1 and C2, is significantly elongated. The aromatic ring is clearly distorted with regard to the bond angles, the *ipso* bond angle at C1 being some 6° smaller than that at C2. The ring also deviates slightly from planarity towards a boat conformation, with a maximum deviation of 0.040 (6) Å for atoms C3 and C6, and, in the opposite direction, of −0.047 (6) Å for atoms C2 and C5. The methylene atom C7 lies almost in the phenyl ring plane, deviating by only 0.0061 (14) Å, whereas the N atom of the nitro group, N2, lies −0.0346 (13) Å below this plane. The N atom of the cyano group, N1, lies 2.1375 (17) Å from the phenyl plane. Although the NO_2/Ar (C1—C2—N2—O2) and CH_2CN/Ar (C2—C1—C7—C8) torsion angles assume their largest values in (I), compared with those in (II) and (III), atom O2 still lies only a mere 2.38 Å from H7*A*, with an O2···H7*A*—C7 angle of 100°.

The question then arises as to whether there is an interaction between nitro atom O2 and methylene atom H7*A*, *cf.* the classical work on 2-nitrobenzaldehyde (Coppens, 1964). The nitro group in (I) is tilted away from the CH_2CN group, as the C1—C2—N2 bond angle is distinctly larger than that of C3—C2—N2, while in (II) and (III), the corresponding angles to the nitro group are similar within experimental error. Likewise, the C2—C1—C7 angle is some 8.6° larger than the C6—C1—C7 angle. This suggests that there is no true intramolecular contact between O2 and the methylene group, even though the O2···C7 distance is also quite short [2.7351 (14) Å]. In the 2-nitrophenylhydrazone of benzaldehyde, the corresponding C1—C2—N2 bond angle is, on the contrary, diminished to 117°, suggesting that an intramolecular H(N)···O(NO_2) interaction is present (Drew *et al.*, 1984; Drew & Willey, 1986). Nonetheless, it is notable that (I) does not fully exploit all its degrees of freedom in reducing these interactions, as the nitro group is still only moderately tilted out of the plane of the phenyl ring.

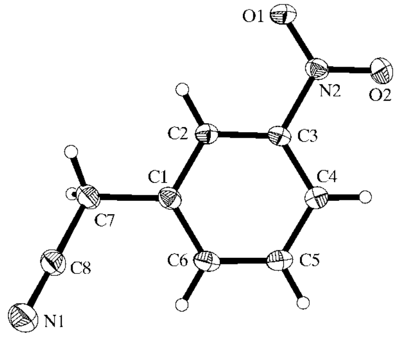


Figure 2
The molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

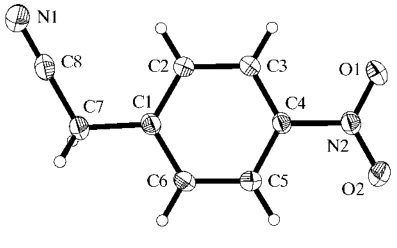


Figure 3
The molecular structure of (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The crystal lattice of (I) is built up by a number of weak intermolecular contacts (Fig. 4), the strongest being N1(CN)···H7*B* and O1···H3, together with the weaker interactions N1···H7*A* and O2···H5, forming several multimembered ring systems. One may also mention the presence of a symmetrical four-membered ring system due to weak N2···O1(−*x*, −*y*, 1 − *z*) contacts of 3.0473 (12) Å, only slightly less than the sum of the van der Waals radii (3.07 Å). There is no evidence for N(CN)···H(Ar) contacts, *π*–*π* stacking or H···*π* interactions.

For (3-nitrophenyl)acetonitrile, (II), the bond lengths and angles are again as expected, the internal angle at C3 being significantly larger than that at C1. This is in agreement with the general rule that the C atom bearing the most electronegative substituent has the larger *ipso* bond angle, *cf.* the Hammet σ values for NO_2 (σ_m = 0.71 and σ_p = 0.81) and CH_2CN (σ_m = 0.16 and σ_p = 0.18) (Isaacs, 1987). The phenyl ring is essentially planar, with maximum and minimum deviations of 0.0082 (6) and −0.0070 (6) Å for atoms C4 and C3, respectively. Atoms C7 [−0.0261 (15) Å] and N2 [−0.0422 (13) Å] are both below this plane and located opposite the cyano group, with a deviation of 1.246 (2) Å for

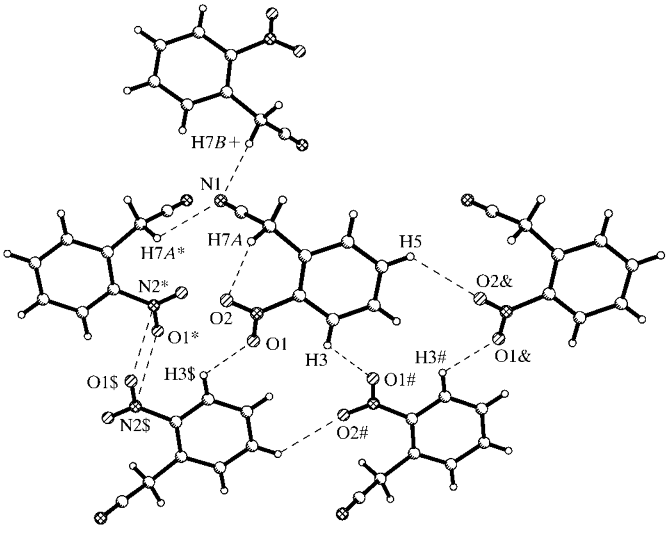


Figure 4
An illustration down [010] (with [001] upwards) of the short contacts in (I). Atoms labelled with an asterisk (*) lie at positions $(-\frac{1}{2} - x, \frac{1}{2} + y, z)$, a plus sign (+) at $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$, a dollar sign ($) at $(x - \frac{1}{2}, \frac{1}{2} - y, 1 - z)$, a hash (#) at $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ and an ampersand (&) at $(1 + x, y, z)$. The unit-cell outline has been omitted for clarity.

atom N1. The strongest intermolecular contacts (Fig. 5) are between the H2 atom *ortho* to the nitro group and atom O1, forming a ten-membered cyclic arrangement, and between atoms O2 and H5. All other interactions, including N(CN)$\cdots$H(CH_2) and N(CN)$\cdots$ H(Ar), are very weak, but some cyclic arrangements seem to be recurrent, *e.g.* N1$\cdots$H6. Again, there is no evidence for H$\cdots\pi$ or π–π interactions.

For (4-nitrophenyl)acetonitrile, (III), as in (II), nitro atom N2 and methylene atom C7 are located opposite the cyano group, deviating from the phenyl-ring plane by −0.0547 (13) and −0.0727 (15) Å, respectively, compared with 0.5325 (19) Å for N1. Both atoms C1 and C4 lie below the plane of the ring, by −0.0082 (6) and −0.0079 (6) Å, respectively, whereas atoms C2 and C5 lie above, by 0.0079 (6) and 0.0074 (6) Å, respectively. Otherwise, all bond lengths and angles in the phenyl group are as expected for a compound with two *para*-substituted groups, both being electron withdrawing (Di Rienzo *et al.*, 1980). The strongest intermolecular contacts, between atom O2 and the aromatic H5 atom *ortho* to the most electronegative substituent, form a cyclic system (Fig. 6). A slightly weaker contact is present between atoms O1 and H6, *ortho* to the least electronegative substituent. As in (I), the cyano N atom in (III) is bifurcated, making contacts with both methylene atom H7*B* and atom H3. A fairly short O1$\cdots$H7*A* distance suggests that atom O1 may also be bifurcated. As found for (I) and (II), no H$\cdots\pi$ or π–π interactions can be detected in (III).

A common characteristic of these three compounds is that the O atoms seem to prefer intermolecular interactions with the aromatic H atoms, the strongest being with the H atom located *ortho* to the nitro group. Notably, none of the O$\cdots$H(CH_2) distances in the three compounds are less than the sum of the van der Waals radii (2.72 Å), despite the known acidity of this class of compounds (Bordwell, 1988). The cyano N atoms, however, show the opposite behaviour, with the N$\cdots$H(CH_2) distances in (I) and (III) being slightly but significantly less than the sum of the van der Waals radii (2.75 Å). Only in (III) is there an N(CN)$\cdots$H contact with an aromatic H atom (H3), but this contact is distinctly weaker than the O$\cdots$H(Ar) contacts. These apparent preferences of the O atoms for the aromatic H atoms and of the cyano N atom for the acidic methylene H atoms are, in principle, as observed for the F$\cdots$H(Ar) and N$\cdots$H(CH_2) interactions in [4-(trifluoromethyl)phenyl]acetonitrile (Boitsov *et al.*, 2002); the O$\cdots$H(Ar) interactions, however, are slightly stronger than the F$\cdots$H(Ar) interactions, as judged from the O$\cdots$H and F$\cdots$H distances.

One may further note that the O1$\cdots$C8($x, -\frac{1}{2} - y, \frac{1}{2} + z$) distance in (III) is fairly short [3.058 (12) Å] compared with the sum of the van der Waals radii (3.22 Å), suggesting some residual positive charge on the cyano C atom, making it a better acceptor when the nitro group is located in the 4-position. The crystal lattice in (II) is essentially built up by two fairly strong O$\cdots$H(Ar) interactions only, compared with one strong interaction assisted by weaker N$\cdots$H(CH_2) interactions in (I) and (III). Consequently, the calculated density of the crystal of (II) (1.453 Mg m^{-3}) is greater than those of (I) and (III) (1.442 and 1.427 Mg m^{-3}, respectively). It should be emphasized that only a few of the bond angles at the H atoms in the intermolecular contacts considered here are close to 180° (Tables 2, 4 and 6). Presumably, the presence of two electronegative substituents will efficiently reduce the ability of the aromatic ring to act as a donor. One may therefore conclude that only in the case of (I) will the cyano N atom be able to compete with the O atoms in initiating the crystallization process.

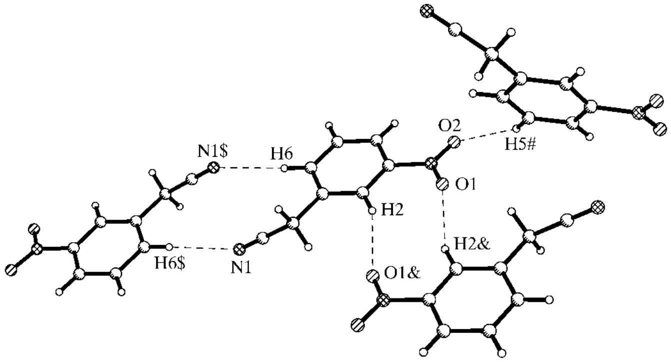


Figure 5
An illustration down [100] (with [010] upwards) of the short contacts in (II). Atoms labelled with an ampersand (&) lie at positions $(-x, -y, 1 - z)$, a dollar sign ($) at $(1 - x, -y, -z)$ and a hash (#) at $(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z)$. The unit-cell outline has been omitted for clarity.

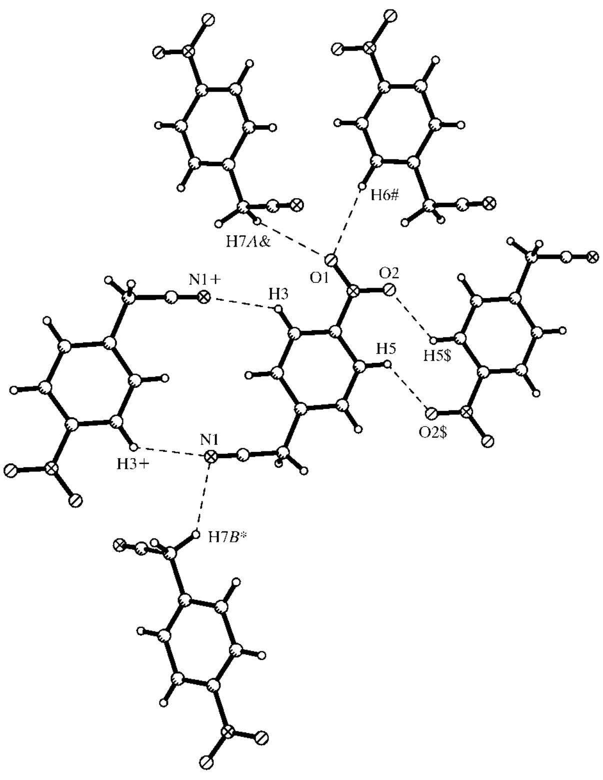


Figure 6
An illustration down [100] (with [001] upwards) of the short contacts in (III). Atoms labelled with an asterisk (*) lie at positions $(2 - x, y - \frac{1}{2}, -\frac{1}{2} - z)$, a plus sign (+) at $(2 - x, -1 - y, -z)$, a dollar sign ($) at $(1 - x, 1 - y, -z)$, a hash (#) at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ and an ampersand (&) at $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$. The unit-cell outline has been omitted for clarity.

Experimental

(2-Nitrophenyl)acetonitrile (purchased from Aldrich, 98%) was dissolved in a minimum volume of diethyl ether at room temperature; cyclohexane was added to the point of turbidity. After filtration, the solution was left at room temperature overnight. The pale-yellow crystals of (I) were washed with cold cyclohexane and dried *in vacuo* (m.p. 354–355 K). Spectroscopic analysis, IR (Nujol, cm^{-1}): 2149 ($C\equiv N$); ^{13}C NMR (600 MHz, $CDCl_3$, δ, p.p.m.): 125.87 (C1), 147.58 (C2), 125.87 (C3), 129.67 (C4), 134.46 (C5), 131.11 (C6), 22.77 (C7), 116.32 (C8); ^1H NMR (600 MHz, $CDCl_3$, δ, p.p.m.): 8.19 (H3), 7.58 (H4), 7.73 (unresolved, H5), 7.74 (unresolved, H6), 4.22 (H7).

(3-Nitrophenyl)acetonitrile (purchased from Aldrich, 99%) was treated similarly to (I), but hexane had to be added to obtain colourless crystals of (II) at 275 K after ~2 h (m.p. 335–336 K). Spectroscopic analysis, IR (Nujol, cm^{-1}): 2149 ($C\equiv N$); ^{13}C NMR (600 MHz, $CDCl_3$, δ, p.p.m.): 133.95 (C1), 123.33 (C2), 148.63 (C3), 123.11 (C4), 130.35 (C5), 131.99 (C6), 23.46 (C7), 116.57 (C8); ^1H NMR (600 MHz, $CDCl_3$, δ, p.p.m.): 8.23 (H2), 8.23 (H4), 7.62 (H5), 7.73 (H6), 3.90 (H7).

(4 Nitrophenyl)acetonitrile (purchased from Aldrich, 98%) was dissolved in a minimum amount of acetone and the solution was filtered after cooling. An equal volume of diethyl ether was then added and suitable pale-yellow crystals of (III) were obtained after ~2 h at 253 K (m.p. 387–388 K). Spectroscopic analysis, IR (Nujol, cm^{-1}): 2149 ($C\equiv N$); ^{13}C NMR (600 MHz, $CDCl_3$, δ, p.p.m.): 137.00 (C1), 128.97 (C2), 124.38 (C3), 147.85 (C4), 124.38 (C5), 128.97 (C6), 23.61 (C7), 116.42 (C8); ^1H NMR (600 MHz, $CDCl_3$, δ, p.p.m.): 7.55 (H2), 8.27 (H3), 8.27 (H5), 7.55 (H6), 3.89 (H7).

Compound (I)

Crystal data

$C_8H_6N_2O_2$
$M_r = 162.15$
Orthorhombic, *Pbca*
$a = 7.9689$ (11) Å
$b = 7.6030$ (8) Å
$c = 24.654$ (3) Å
$V = 1493.7$ (3) Å^3
$Z = 8$
$D_x = 1.442$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 3.0$–31.5°
$\mu = 0.11$ mm^{-1}
$T = 123$ (2) K
Flat prism, pale yellow
0.48 × 0.43 × 0.06 mm

Data collection

Bruker SMART 2K CCD area-detector diffractometer
ω scans
Absorption correction: numerical (*SHELXTL*/*PC*; Sheldrick, 2001*a*)
$T_{min} = 0.943$, $T_{max} = 0.994$
25 225 measured reflections
2494 independent reflections
2083 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 31.5°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -36 \rightarrow 36$
220 standard reflections, remeasured at the end of data collection after ~28 h intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.123$
$S = 1.08$
2494 reflections
109 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0791P)^2 + 0.1627P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C1—C2	1.4026 (12)	O2—N2	1.2314 (12)
C1—C7	1.5162 (12)	C2—N2	1.4720 (11)
N1—C8	1.1426 (12)	C7—C8	1.4693 (13)
O1—N2	1.2258 (11)		
C2—C1—C6	116.44 (8)	O1—N2—C2	118.29 (8)
C2—C1—C7	126.09 (8)	O1—N2—O2	123.53 (8)
C6—C1—C7	117.47 (8)	O2—N2—C2	118.15 (8)
C1—C2—C3	122.71 (8)	C1—C7—C8	113.47 (7)
C1—C2—N2	121.31 (7)	N1—C8—C7	178.40 (10)
C3—C2—N2	115.98 (8)		
C1—C2—N2—O2	−19.83 (13)	C2—C1—C7—C8	−62.27 (12)

Table 2
Short-contact geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O1^{i}	0.95	2.54	3.1982 (11)	127
C5—H5···O2^{ii}	0.95	2.62	3.2876 (13)	127
C7—H7*A*···O2	0.99	2.38	2.7351 (14)	100
C7—H7*A*···N1^{iii}	0.99	2.66	3.2904 (13)	122
C7—H7*B*···N1^{iv}	0.99	2.50	3.4877 (13)	172

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (ii) $1+x, y, z$; (iii) $-\frac{1}{2}-x, y-\frac{1}{2}, z$; (iv) $-x, y-\frac{1}{2}, \frac{3}{2}-z$.

Compound (II)

Crystal data

$C_8H_6N_2O_2$
$M_r = 162.15$
Monoclinic, $P2_1/n$
$a = 5.3641$ (4) Å
$b = 11.5157$ (9) Å
$c = 12.1981$ (10) Å
$\beta = 100.369$ (2)°
$V = 741.19$ (10) Å^3
$Z = 4$
$D_x = 1.453$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6347 reflections
$\theta = 2.5$–31.6°
$\mu = 0.11$ mm^{-1}
$T = 123$ (2) K
Irregular prism, colourless
0.50 × 0.30 × 0.08 mm

Data collection

Bruker SMART 2K CCD area-detector diffractometer
ω scans
Absorption correction: numerical (*SHELXTL*/*PC*; Sheldrick, 2001*a*)
$T_{min} = 0.958$, $T_{max} = 0.992$
12 917 measured reflections
2463 independent reflections
2005 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 31.6°$
$h = -7 \rightarrow 7$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 17$
155 standard reflections, remeasured at the end of data collection after ~28 h intensity: none

Table 3
Selected geometric parameters (Å, °) for (II).

C1—C7	1.5161 (13)	O2—N2	1.2311 (10)
N1—C8	1.1460 (13)	C7—C8	1.4687 (13)
O1—N2	1.2296 (10)		
C2—C1—C6	119.44 (8)	C2—C3—C4	123.31 (8)
C2—C1—C7	118.55 (8)	C2—C3—N2	118.12 (8)
C6—C1—C7	121.97 (8)	C4—C3—N2	118.57 (8)
O1—N2—O2	123.30 (8)	C1—C7—C8	113.41 (8)
O1—N2—C3	118.58 (7)	N1—C8—C7	178.98 (11)
O2—N2—C3	118.12 (7)		
C2—C3—N2—O1	−5.69 (12)	C2—C1—C7—C8	−147.99 (9)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.118$
$S = 1.09$
2463 reflections
109 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0699P)^2 + 0.0827P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 4
Short-contact geometry (Å, °) for (II).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C2—H2⋯O1^{i}	0.95	2.51	3.4010 (11)	157
C5—H5⋯O2^{ii}	0.95	2.55	3.4009 (11)	150
C6—H6⋯N1^{iii}	0.95	2.73	3.6806 (13)	174

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $1-x, -y, -z$.

Compound (III)

Crystal data

$C_8H_6N_2O_2$
$M_r = 162.15$
Monoclinic, $P2_1/c$
$a = 8.1695$ (7) Å
$b = 5.9775$ (5) Å
$c = 15.7260$ (13) Å
$\beta = 100.695$ (2)°
$V = 754.61$ (11) Å^3
$Z = 4$

$D_x = 1.427$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7016 reflections
$\theta = 2.5$–31.5°
$\mu = 0.11$ mm^{-1}
$T = 123$ (2) K
Flat prism, pale yellow
0.40 × 0.30 × 0.11 mm

Data collection

Bruker SMART 2K CCD area-detector diffractometer
ω scans
Absorption correction: numerical (*SHELXTL/PC*; Sheldrick, 2001*a*)
$T_{\min} = 0.965$, $T_{\max} = 0.989$
13 089 measured reflections
2489 independent reflections
2097 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.022$
$\theta_{\max} = 31.5°$
$h = -11 \rightarrow 11$
$k = -8 \rightarrow 8$
$l = -23 \rightarrow 23$
140 standard reflections, remeasured at the end of ata collection after ~28 h
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.120$
$S = 1.08$
2489 reflections
109 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0734P)^2 + 0.0923P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III).

C1—C7	1.5179 (12)	O2—N2	1.2317 (10)
N1—C8	1.1431 (13)	N2—C4	1.4720 (11)
O1—N2	1.2288 (10)	C7—C8	1.4659 (13)
C2—C1—C7	122.70 (8)	C3—C4—N2	119.03 (7)
C6—C1—C7	117.67 (7)	C5—C4—N2	118.51 (7)
O1—N2—O2	123.05 (8)	C1—C7—C8	114.05 (7)
O1—N2—C4	118.34 (7)	N1—C8—C7	179.54 (10)
O2—N2—C4	118.60 (7)		
C2—C1—C7—C8	−16.75 (14)	C3—C4—N2—O1	−2.88 (12)

Table 6
Short-contact geometry (Å, °) for (III).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3⋯N1^{i}	0.95	2.65	3.3459 (12)	130
C5—H5⋯O2^{ii}	0.95	2.55	3.2520 (11)	131
C6—H6⋯O1^{iii}	0.95	2.60	3.5262 (11)	165
C7—H7*A*⋯O1^{iv}	0.99	2.72	3.3528 (13)	122
C7—H7*B*⋯N1^{v}	0.99	2.61	3.4040 (13)	137

Symmetry codes: (i) $2-x, -1-y, -z$; (ii) $1-x, 1-y, -z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $x, -\frac{1}{2}-y, z-\frac{1}{2}$; (v) $2-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

H atoms were treated as riding atoms, with C—H(CH) and C—H(CH_2) distances of 0.95 and 0.99 Å, respectively, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$ of their parent atoms. The maximum residual peak is located 0.82 Å from O2 in (I), 0.69 Å from C2 in (II) and 0.69 Å from C4 in (III).

For all compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 2001*b*); molecular graphics: *SHELXTL/PC* (Sheldrick, 2001*a*); software used to prepare material for publication: *SHELXTL/PC* and *PLATON* (Spek, 2001).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1652). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Boitsov, S., Songstad, J. & Törnroos, K. W. (2002). *Acta Cryst.* C**58**, o145–o147.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bordwell, F. G. (1988). *Acc. Chem. Res.* **21**, 456–463.
Bruker (1999). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SAINT*. Version 6.02a. Bruker AXS Inc., Madison, Wisconsin, USA.
Coppens, P. (1964). *Acta Cryst.* **17**, 573–578.
Desiraju, G. R. & Steiner, T. (1999). Editors. *The Weak Hydrogen Bond*. Oxford University Press.
Di Rienzo, F., Domenicano, A. & Riva di Sanseverino, L. (1980). *Acta Cryst.* B**36**, 586–591.
Drew, M. G. B., Vickery, B. & Willey, G. R. (1984). *Acta Cryst.* C**40**, 304–306.
Drew, M. G. B. & Willey, G. R. (1986). *J. Chem. Soc. Perkin Trans.* 2, pp. 215–220.
Dunitz, J. D. (1991). *Pure Appl. Chem.* **63**, 177–185.
Goubitz, K., Sonneveld, E. J., Chernyshev, V. V., Yatsenko, A. V., Zhukov, S. G., Reiss, C. A. & Schenk, H. (1999). *Z. Kristallogr.* **214**, 469–474.
Higashi, T. & Osaki, K. (1977). *Acta Cryst.* B**33**, 2337–2339.
Isaacs, N. S. (1987). *Physical Organic Chemistry*, pp. 134–135. London: Longman Group UK Ltd.
Jaiboon, N., Chaichit, N., Pipoosananakaton, B., Tuntulani, T. & Sukwattanasinitt, M. (2001). *J. Chem. Crystallogr.* **30**, 717–720.
Lehn, J.-M. (1995). *Supramolecular Chemistry: Concepts and Perspectives*. Weinheim: VCH.
Nishide, K., Hagimoto, Y., Hasegawa, H., Shiro, M. & Node, M. (2001). *Chem. Commun.* pp. 2394–2395.
Schweizer, W. B., Procter, G., Kaftory, M. & Dunitz, J. D. (1978). *Helv. Chim. Acta*, **61**, 2783–2808.
Seiler, P. & Dunitz, J. D. (1989). *Helv. Chim. Acta*, **72**, 1125–1135.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (2001*a*). *SHELXTL/PC*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2001*b*). *SHELXL*97. University of Göttingen, Germany.
Shimon, L. J. W., Vaida, M., Addadi, L., Lahav, M. & Leiserowitz, L. (1990). *J. Am. Chem. Soc.* **112**, 6215–6220.
Spek, A. L. (2001). *PLATON*. University of Utrecht, The Netherlands.
Thalladi, V. R., Weiss, H.-C., Bläser, D., Boese, R., Nangia, A. & Desiraju, G. R. (1998). *J. Am. Chem. Soc.* **120**, 8702–8710.