

Cyano–cyano and chloro–cyano interactions in two imidazole derivatives

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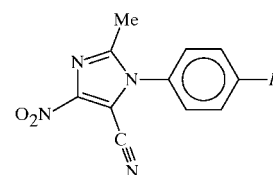
In two closely related 1-aryl-2-methyl-4-nitro-5-cyanoimidazoles, namely 2-methyl-4-nitro-1-phenyl-1*H*-imidazole-5-carbonitrile, $C_{11}H_8N_4O_2$, and 1-(4-chlorophenyl)-2-methyl-4-nitro-1*H*-imidazole-5-carbonitrile, $C_{11}H_7ClN_4O_2$, different weak intermolecular interactions determine the crystal packing. In the 1-phenyl derivative, dipole–dipole interactions between antiparallel cyano groups connect molecules into centrosymmetric dimers, while in the 1-(4-chlorophenyl) derivative, the dimers are connected by $C\equiv N\cdots Cl-C$ halogen bonds. These interactions, together with weak $C-H\cdots O(N)$ hydrogen bonds, connect molecules related by subsequent centres of inversion into infinite tapes.

Comment

Weak intermolecular interactions play a decisive role in determining the three-dimensional structure of molecular crystals. Hydrogen bonds are by far the most important – and best known – of these interactions, but in the absence of strong hydrogen-bond donors or acceptors (or sometimes in spite of their presence), other weak interactions stabilize certain structures. The list of these interactions is long and still growing.

Among these, the attractive interaction between a carbon-bound halogen atom and atoms having electron lone pairs has been known for some time (Hassel & Rømming, 1962; Hassel, 1970). This interaction has been termed ‘halogen bonding’ (Dumas *et al.*, 1983; Legon, 1998) in order to stress the analogy with hydrogen bonding [for recent reviews see, for example, Legon (1999), Metrangolo & Resnati (2001) and Metrangolo *et al.* (2003)]. The reorganization of electron-density distribution connected with this interaction is directed from a Lewis base electron-donor site to the halogen atom, which acts as a Lewis acid. The acidity scale $I > Br > Cl$ (for fluorine there is no detectable tendency to form this type of interaction) was established on the basis of Cambridge Structural Database (Allen, 2002) studies (Lommerse *et al.*, 1996) and quantum-chemical calculations (Valerio *et al.*, 2000). A special case of

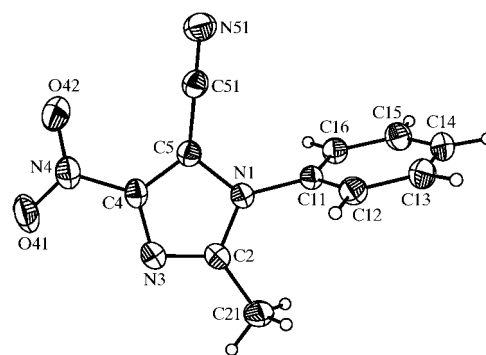
this interaction involves the cyano group as an electron donor. The existence of short $C\equiv N\cdots X-C$ contacts was postulated over 40 years ago (Hassel & Rømming, 1962) and confirmed by the structures of some simple cyano–halogen compounds (Witt *et al.*, 1972). The role of cyano–halogen interactions in the crystal structures of 4-halobenzonitriles was described by Desiraju & Harlow (1989), and $C\equiv N\cdots Cl-C$ halogen bonds were used as the supramolecular synthon [as defined by Desiraju (1995)] to create linear zigzag arrays of flat molecules (molecular tapes; Reddy *et al.*, 1993). These contacts were also identified in a series of tetrachlorodicyanobenzenes (Britton, 2002, and references therein).

(I) $R = H$ (II) $R = Cl$

In addition, the cyano group can accept hydrogen bonds (Ziao *et al.*, 2001) and can take part in dipole–dipole interactions, analogous to the carbonyl–carbonyl interactions that have been found to be able to compete successfully with hydrogen bonds (Allen *et al.*, 1998).

In the course of studies of weak interactions in nitroimidazoles (Kubicki *et al.*, 2001, 2002), the crystal structures of two closely related 5-cyano derivatives, namely 2-methyl-4-nitro-1-phenyl-1*H*-imidazole-5-carbonitrile, (I), and 1-(4-chlorophenyl)-2-methyl-4-nitro-1*H*-imidazole-5-carbonitrile, (II), have been determined. Because of the lack of strong hydrogen-bond donors, these compounds offer the opportunity of comparing the weak interactions described above.

Figs. 1 and 2 show anisotropic displacement-ellipsoid representations of the molecules of (I) and (II), respectively. The bond lengths and angles are almost identical; the only (and obvious) differences are related to the presence of the Cl substituent in (II). This substituent causes modest changes in the intra-annular bond angles of the benzene ring, in general agreement with those described by Domenicano & Murray-

**Figure 1**

A view of the molecule of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are depicted as spheres of arbitrary radii.

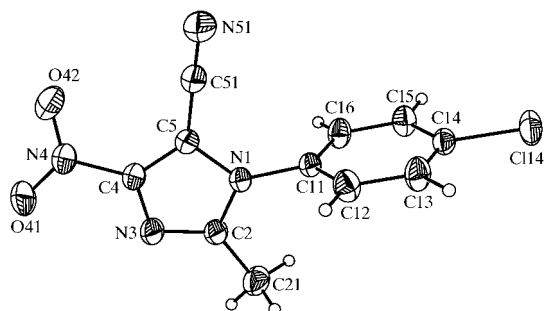


Figure 2
A view of the molecule of (II). Displacement ellipsoids are drawn at the 30% probability level and H atoms are depicted as spheres of arbitrary radii.

Rust (1979) for monosubstituted benzene derivatives; in chloro derivative (II), the angle at the site of substitution (C13–C14–C15) is larger and the two adjacent angles (C12–C13–C14 and C14–C15–C16; Tables 1 and 3) are smaller than the equivalent angles in (I).

The conformations of (I) and (II) are slightly different. The dihedral angles involving the three effectively planar fragments, *viz.* the imidazole ring (*A*), the benzene ring (*B*) and the nitro group (*C*), are larger in (II); the angle between planes *A* and *B* is 87.64 (6)° in (II) and 76.29 (4)° in (I), and the angle between planes *A* and *C* is 7.65 (2)° in (II) and 0.59 (13)° in (I).

In the crystal structure of (I), relatively short contacts exist between antiparallel C≡N groups of molecules related by a centre of inversion. The distance between the mid-points of these bonds is 3.271 (2) Å and the C5–C51···N51 angle is 82.9 (1)°. These dipole–dipole interactions lead to the formation of centrosymmetric dimers in (I). The only other intermolecular interaction that plays a role in the crystal packing is the weak C12–H12···O41(1–*x*, –*y*, 1–*z*) hydrogen bond (Table 2), which also closes the dimers related by another centre of inversion (Fig. 3).

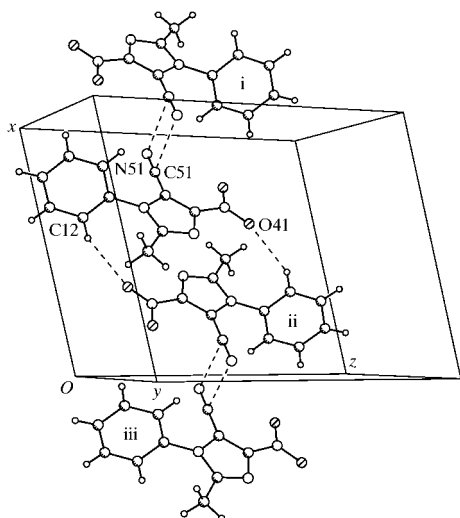


Figure 3
The chain of molecules of (I) connected by dipole–dipole and C–H···O interactions, viewed approximately along the [010] direction. [Symmetry codes: (i) 2–*x*, –*y*, 1–*z*; (ii) 1–*x*, –*y*, 1–*z*; (iii) –1+*x*, *y*, *z*.]

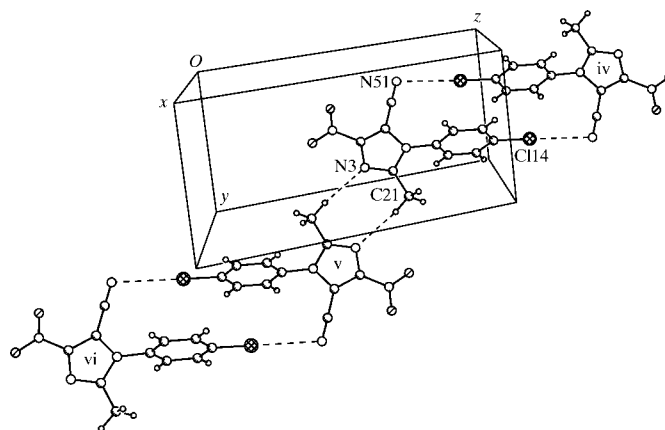


Figure 4
The chain of molecules of (II) connected by C≡N···Cl–C and C–H···N interactions, viewed approximately along the [100] direction. [Symmetry codes: (iv) 1–*x*, 1–*y*, 2–*z*; (v) 1–*x*, 2–*y*, 1–*z*; (vi) *x*, 1+*y*, –1+*z*.]

In (II), the presence of the Cl atom changes the hierarchy of intermolecular interactions. In this case, the main driving force of crystal packing is the C–Cl···N≡C interaction, which also closes the centrosymmetric dimers (Fig. 4). The Cl···N distance is short but typical for this kind of interaction [3.250 (2) Å], and the linearity of the C–Cl···N contact [168.30 (8)°] testifies to the proposed mechanism of charge donation (the donation of the lone pair to the σ -antibonding orbital of C–X). The C–H···N hydrogen bonds (Table 4) between neighboring molecules (connected by another centre of inversion) also take part in the crystal packing (Fig. 4).

There are some similarities in the crystal-packing modes of (I) and (II). In both cases, the structure consists of tapes of molecules connected by alternating pairs of weak interactions [\sim dipole–dipole \sim C–H···O \sim in (I) and \sim C≡N···Cl–C \sim C–H···N \sim in (II)], and these tapes utilize the consecutive centres of inversion. No other symmetry elements are used in creating the principal packing motifs, even though the space group ($P2_1/n$) contains such elements.

Experimental

The methods of synthesis of (I) and (II) were described by Salwińska & Suwiński (1990) and Suwiński *et al.* (1994). Crystals suitable for data collection were grown from methanol solutions.

Compound (I)

Crystal data

C₁₁H₈N₄O₂
M_r = 228.21
 Monoclinic, $P2_1/n$
a = 9.8976 (9) Å
b = 9.6168 (9) Å
c = 11.6700 (10) Å
 β = 103.313 (7)°
V = 1080.94 (17) Å³
Z = 4
D_x = 1.402 Mg m^{–3}

Mo *K* α radiation
 Cell parameters from 2418 reflections
 θ = 3–21°
 μ = 0.10 mm^{–1}
T = 293 (2) K
 Prism, colourless
 0.30 × 0.25 × 0.15 mm

Data collection

Kuma KM-4 CCD four-circle diffractometer
 ω scans
 6917 measured reflections
 2708 independent reflections
 1380 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 29.3^\circ$
 $h = -13 \rightarrow 11$
 $k = -11 \rightarrow 13$
 $l = -14 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.093$
 $S = 0.91$
 2708 reflections
 176 parameters
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.11 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$

Table 1

Selected bond angles ($^\circ$) for (I).

C12—C13—C14	120.5 (2)	C14—C15—C16	120.2 (2)
C13—C14—C15	120.4 (2)		

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C12—H12 \cdots O41 ⁱⁱ	0.95 (2)	2.59 (2)	3.456 (2)	151 (1)

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

Compound (II)

Crystal data

$\text{C}_{11}\text{H}_7\text{ClN}_4\text{O}_2$
 $M_r = 262.66$
 Monoclinic, $P2_1/n$
 $a = 12.6819 (16) \text{\AA}$
 $b = 6.8018 (11) \text{\AA}$
 $c = 15.1799 (16) \text{\AA}$
 $\beta = 114.497 (11)^\circ$
 $V = 1191.5 (3) \text{\AA}^3$
 $Z = 4$
 $D_x = 1.464 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 2798 reflections
 $\theta = 3-18^\circ$
 $\mu = 0.32 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Plate, colourless
 $0.6 \times 0.5 \times 0.1 \text{ mm}$

Data collection

Kuma KM-4 CCD four-circle diffractometer
 ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1989)
 $T_{\text{min}} = 0.889, T_{\text{max}} = 0.971$
 7375 measured reflections

2968 independent reflections
 1647 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\text{max}} = 29.3^\circ$
 $h = -17 \rightarrow 15$
 $k = -9 \rightarrow 6$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.102$
 $S = 0.97$
 2968 reflections
 182 parameters
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.045P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.17 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.011 (2)

The positional parameters of the H atoms of the aryl groups were refined isotropically, giving C—H distances in the range 0.89 (2)–0.97 (3) \AA . Methyl H atoms were treated as riding, with C—H distances of 0.96 \AA .

Table 3

Selected bond angles ($^\circ$) for (II).

C12—C13—C14	119.00 (18)	C14—C15—C16	119.32 (19)
C13—C14—C15	121.36 (16)		

Table 4

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C21—H21A \cdots O41 ^{vii}	0.96	2.61	3.392 (3)	139
C21—H21C \cdots N3 ^v	0.96	2.53	3.479 (3)	171

Symmetry codes: (v) $1 - x, 2 - y, 1 - z$; (vii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1304). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Allen, F. H., Baalham, C. A., Lommerse, J. P. M. & Raithby, P. R. (1998). *Acta Cryst.* **B54**, 320–329.
 Blessing, R. H. (1989). *J. Appl. Cryst.* **22**, 396–397.
 Britton, D. (2002). *Acta Cryst.* **B58**, 553–563.
 Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
 Desiraju, G. R. & Harlow, R. L. (1989). *J. Am. Chem. Soc.* **111**, 6757–6764.
 Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* **24**, 2283–2286.
 Dumas, J. M., Gomel, L. & Guerin, M. (1983). *The Chemistry of Functional Groups*, Suppl. D, edited by S. Patai & Z. Rappaport, pp. 985–1020. New York: Wiley.
 Hassel, O. (1970). *Science*, **170**, 497–502.
 Hassel, O. & Rømming, C. (1962). *Q. Rev. Chem. Soc.* **16**, 1–13.
 Kubicki, M., Borowiak, T., Dutkiewicz, G., Souhassou, M., Jelsch, C. & Lecomte, C. (2002). *J. Phys. Chem. B*, **106**, 3706–3714.
 Kubicki, M., Borowiak, T., Suwiński, J. & Wagner, P. (2001). *Acta Cryst.* **C57**, 106–108.
 Legon, A. C. (1998). *Chem. Eur. J.* **4**, 1890–1897.
 Legon, A. C. (1999). *Angew. Chem. Int. Ed.* **38**, 2687–2714.
 Lommerse, J. P. M., Stone, A. J., Taylor, R. & Allen, F. H. (1996). *J. Am. Chem. Soc.* **118**, 3108–3116.
 Metrangolo, P., Pilati, T., Resnati, G. & Stevenazzi, A. (2003). *Curr. Opin. Colloid Interface Sci.* **8**, 215–222.
 Metrangolo, P. & Resnati, G. (2001). *Chem. Eur. J.* **7**, 2511–2519.
 Oxford Diffraction (2002). *CrysAlis CCD* and *CrysAlis RED*. Versions 169. Oxford Diffraction, Wroclaw, Poland.
 Reddy, D. S., Panneerselvam, K., Pilati, T. & Desiraju, G. R. (1993). *J. Chem. Soc. Chem. Commun.* pp. 661–662.
 Salwińska, E. & Suwiński, J. (1990). *Pol. J. Chem.* **64**, 813–820.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Siemens (1989). *Stereochemical Workstation Operation Manual*. Release 3.4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Suwiński, J., Szczepankiewicz, W. & Wagner, P. (1994). *Pol. J. Appl. Chem.* **38**, 499–510.
 Valerio, G., Raos, G., Meille, S. V., Metrangolo, P. & Resnati, G. (2000). *J. Phys. Chem. A*, **104**, 1617–1620.
 Witt, J. R., Britton, D. & Mahon, C. (1972). *Acta Cryst.* **B28**, 950–955.
 Ziao, N., Graton, J., Laurence, C. & LeQuestel, J.-Y. (2001). *Acta Cryst.* **B57**, 850–858.