

1-(4-Bromophenyl)-2-methyl-4-nitro-1*H*-imidazole: bifurcated Br···O halogen–nitro bonds

Maciej Kubicki

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6,
60-780 Poznań, Poland

Correspondence e-mail: mkubicki@amu.edu.pl

Received 16 March 2004

Accepted 19 March 2004

Online 21 April 2004

The crystal packing of the title compound, C₁₀H₈BrN₃O₂, is determined mainly by relatively strong bifurcated C—Br···O halogen–nitro bonds. Both O atoms are involved in this interaction in an almost symmetrical manner and the difference [0.078 (3) Å] between the Br···O contact lengths is one of the smallest found in similar compounds. Halogen bonds and weak hydrogen bonds connect molecules into layers which are stacked along the [100] direction.

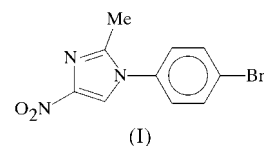
Comment

The attractive interactions between organic halogen (*X*) and nitro-group O atoms have been identified as robust and effective supramolecular synthons, as defined by Desiraju (1995). Allen *et al.* (1997) carried out an analysis of the Cambridge Structural Database (CSD) and an *ab initio* molecular study, which showed that the degree of interpenetration of the *X* and O atoms increases in the order Cl < Br < I, and that the C—*X*···O angle becomes closer to 180° as the *X*···O separation decreases. This is an example of a wider group of so-called ‘halogen bonds’, the attractive interaction between organic halogen and atoms possessing electron lone pairs [for a recent review see, for example, Metrangolo *et al.* (2003)]. This interaction is directional and can compete successfully with hydrogen bonds for the leading role in driving self-assembly processes (Corradi *et al.*, 2000). There are examples of the presence of halogen bonds in liquid crystals (Nguyen *et al.*, 2004), in solution (Wash *et al.*, 1999) and in the gas phase (Legon, 1998).

In the case of the *X*···O halogen–nitro bond, three different motifs have been identified (Desiraju *et al.*, 1993). The first is the symmetrical bifurcated motif, in which the two *X*···O distances are almost equal and *X* effectively interacts with both O atoms. The second is the asymmetrical bifurcated motif, in which one of the *X*···O distances is too long for any interaction, but the *X* atom still approaches the bonded O atoms *trans* to the C—N bond. The third is the monocoor-

inated motif, when the *X*···O contact is *cis* to the C—N bond. Allen *et al.* (1997) found that the tendency to form the bifurcated motif increases in the order Cl < Br < I.

Against this background, and as part of a wider study of weak interactions in 4-nitroimidazole derivatives, the crystal structure of 1-(4-bromophenyl)-2-methyl-4-nitro-1*H*-imidazole, (I), has been determined and the results are presented here.



The crystal packing of (I) could, in principle, be influenced by at least three specific interactions, namely π – π stacking of planar aromatic fragments, weak C—H···O(N) hydrogen bonds and Br···O halogen bonds. All three kinds of interactions have been found in similar compounds (*e.g.* 1-aryl-4-nitro-5-methylimidazole derivatives; Kubicki, 2004).

Fig. 1 shows the molecule of (I), which consists of three planar fragments: the phenyl ring [maximum deviation from the least-squares plane 0.007 (3) Å for atom C14], the imidazole ring [maximum deviation 0.006 (2) Å for atom C5] and the nitro group. The dihedral angle between the phenyl and imidazole ring planes is 56.4 (1)° and the nitro group is almost parallel to the imidazole plane [1.8 (6)°]. The bond lengths and angles are typical.

There is an interesting asymmetry in the geometry of the nitro group. The N—O bond *cis* to atom N3 (N4—O41) is slightly shorter [by 0.013 (4) Å] than the *trans* bond (N4—O42). This asymmetry is accompanied by a difference in the C—N—O angles, with C4—N4—O41 being 2.3 (3)° greater than C4—N4—O42. Exactly the reverse situation was found in the series of 1-aryl-4-nitro-5-methylimidazole derivatives (Kubicki, 2004). A CSD (Version 5.25; Allen, 2002) analysis shows that this can be regarded as a strong tendency: asymmetry similar to that in (I) is observed in simple 1-substituted-4-nitroimidazoles, without the substituent at the 5-position, while in case of 5-substituted compounds, the situation is reversed, with C4—N4—O42-type angles being greater than C4—N4—O41.

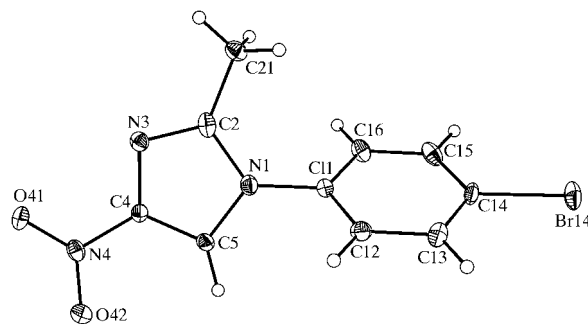


Figure 1

A view of the molecule of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as small spheres of arbitrary radii.

The crystal structure of (I) is determined by relatively short Br...O halogen bonds of the first type mentioned above, *i.e.* almost symmetrical and bifurcated. The Br...O41ⁱ distance is 3.364 (3) Å and Br...O42ⁱⁱ is 3.286 (3) Å [symmetry code: (i) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$]. The difference between these contacts, 0.078 (3) Å, is one of the smallest found in similar compounds. In the January 2004 version of the CSD, there are 111 compounds which have both aromatic Br and nitro groups (only organics, no errors, coordinates available, duplicate entries excluded). In 34 (*ca* 31%) of these structures, the Br...O contact is shorter than the sum of the van der Waals radii. When the limit is set at the sum of the van der Waals radii plus 0.2 Å, the fraction of structures fulfilling this condition grows to almost 43% (47 structures, 66 fragments). Only for 12 of these cases is the difference between Br...O distances less than 0.3 Å. The smallest difference, 0.072 Å, was found in the structure of 1-acetyl-5-bromo-7-nitroindoline (Moreno *et al.*, 1998), and the present case provides the second most symmetrical Br...O(nitro) approach.

This CSD analysis confirms the directionality of this type of interaction and the tendency towards more linear C—Br...O angles as the Br...O separation decreases. In particular, for Br...O distances shorter than 3.33 Å there are no C—Br...O angles smaller than 139°. The case of (I) follows this tendency, with the C—Br...O41 angle being 158.5° and C—Br...O42 157.3°.

These halogen bonds, together with weak C—H...O and C—H...N contacts (Table 2 and Fig. 2), connect the molecules of (I) into layers. Using graph-set notation (Etter *et al.*, 1990; Bernstein *et al.*, 1995), there are first-order chains, C(10)[R₂¹(4)], C(4) and C(7), and more interesting higher-order rings, R₂²(9) and R₄⁴(18). Following, for example, Bryant *et al.* (1998), we have taken the Br...O halogen bonds as pseudo-hydrogen bonds, with Br as the donor and O as the acceptor. These layers are stacked on top of one another, and there are only weak C—H...O contacts between neighbouring layers, as the distance between the ring planes is too long for a significant stacking interaction (4.15 Å).

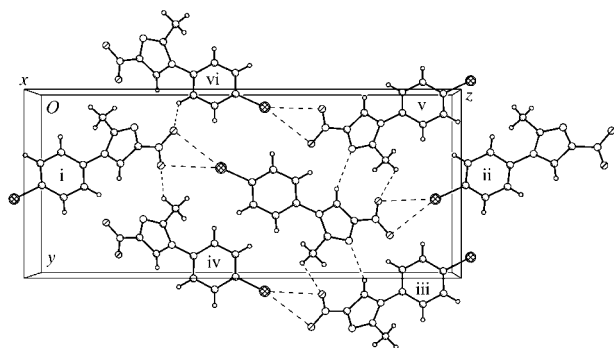


Figure 2
The layer of molecules of (I), as seen along the [100] direction. Halogen bonds and weak hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$; (ii) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$; (iii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iv) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$; (v) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (vi) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.]

Experimental

Compound (I) was synthesized according to the method described elsewhere by Suwiński & Świerczek (1996). Crystals suitable for data collection were grown from a methanol solution by slow evaporation.

Crystal data

C ₁₀ H ₈ BrN ₃ O ₂	Mo K α radiation
<i>M_r</i> = 282.10	Cell parameters from 2848 reflections
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	θ = 3–18°
<i>a</i> = 4.1443 (5) Å	μ = 3.92 mm ⁻¹
<i>b</i> = 10.4459 (8) Å	<i>T</i> = 100 (1) K
<i>c</i> = 24.1758 (19) Å	Prism, colourless
<i>V</i> = 1046.59 (17) Å ³	0.60 × 0.15 × 0.10 mm
<i>Z</i> = 4	
<i>D_x</i> = 1.790 Mg m ⁻³	

Data collection

Kuma KM-4 CCD four-circle diffractometer	1977 reflections with <i>I</i> > 2σ(<i>I</i>)
ω scans	<i>R</i> _{int} = 0.096
Absorption correction: multi-scan (SORTAV; Blessing, 1989)	θ_{max} = 29.2°
<i>T</i> _{min} = 0.389, <i>T</i> _{max} = 0.676	<i>h</i> = -5 → 3
4145 measured reflections	<i>k</i> = -13 → 13
2308 independent reflections	<i>l</i> = -31 → 15

Refinement

Refinement on <i>F</i> ²	(Δ/σ) _{max} = 0.001
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.040	$\Delta\rho_{\text{max}}$ = 0.73 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.097	$\Delta\rho_{\text{min}}$ = -0.95 e Å ⁻³
<i>S</i> = 1.10	Absolute structure: Flack (1983),
2308 reflections	613 Friedel pairs
146 parameters	Flack parameter = -0.018 (15)
H-atom parameters constrained	
<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0539 <i>P</i>) ² + 0.104 <i>P</i>]	
where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3	

Table 1

Selected geometric parameters (Å, °).

N1—C5	1.372 (5)	N3—C4	1.363 (5)
N1—C2	1.389 (5)	C4—N4	1.439 (5)
N1—C11	1.443 (4)	N4—O41	1.224 (4)
C14—Br14	1.900 (4)	N4—O42	1.237 (4)
C2—N3	1.322 (5)		
C5—N1—C2	107.8 (3)	N3—C4—N4	121.0 (3)
C15—C14—C13	120.9 (3)	C5—C4—N4	125.7 (4)
C15—C14—Br14	119.5 (3)	O41—N4—O42	124.2 (3)
C13—C14—Br14	119.6 (3)	O41—N4—C4	119.0 (3)
C2—N3—C4	104.3 (3)	O42—N4—C4	116.7 (3)

Table 2

Hydrogen-bonding and short-contact geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C12—H12...O41 ⁱ	0.95	2.52	3.114 (5)	121
C21—H21A...O42 ⁱⁱ	0.98	2.48	3.026 (5)	115
C21—H21C...O42 ⁱⁱⁱ	0.98	2.62	3.434 (5)	141
C5—H5...N3 ^{iv}	0.95	2.85	3.759 (5)	161

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

The positions of the H atoms were constrained with appropriate AFIX instructions and their U_{iso} values were set at $1.2U_{\text{eq}}$ of the carrier atom ($1.3U_{\text{eq}}$ for the methyl group).

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); software used to prepare material for publication: *SHELXL97*.

The author thanks Dr Paweł Wagner for providing the title compound and for stimulating discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1748). 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., Lommerse, J. P. M., Hoy, V. J., Howard, J. A. K. & Desiraju, G. R. (1997). *Acta Cryst.* **B53**, 1006–1016.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Blessing, R. H. (1989). *J. Appl. Cryst.* **22**, 396–397.
- Bryant, R., James, S. C., Norman, N. C. & Orpen, A. G. (1998). *Acta Cryst.* **C54**, 1113–1115.
- Corradi, E., Meille, S. V., Messina, M. T., Metrangolo, P. & Resnati, G. (2000). *Angew. Chem. Int. Ed.* **39**, 1782–1786.
- Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
- Desiraju, G. R., Pedireddi, V. R., Sarma, J. A. R. P. & Zacharias, D. E. (1993). *Acta Chim. Hung.* **130**, 451–465.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Kubicki, M. (2004). *J. Mol. Struct.* Submitted.
- Legon, A. C. (1998). *Chem. Eur. J.* **4**, 1890–1897.
- Metrangolo, P., Pilat, T., Resnati, G. & Stevenazzi, A. (2003). *Curr. Opin. Colloid Interface Sci.* **8**, 215–222.
- Moreno, M. M. T., Santos, R. H. A., Gambardella, M. T. P., Camargo, A. J., da Silva, A. B. F. & Trsic, M. (1998). *Struct. Chem.* **9**, 365–373.
- Nguyen, H. L., Horton, P. N., Hursthouse, M. B., Legon, A. C. & Bruce, D. W. (2004). *J. Am. Chem. Soc.* **126**, 16–17.
- Oxford Diffraction (2002). *CrysAlis CCD* (Version 1.69) and *CrysAlis RED*. Oxford Diffraction, Wroclaw, Poland.
- 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. & Świerczek, K. (1996). *Khim. Geterosikl. Soedin.* **32**, 1214–1221. (In Russian.)
- Wash, P. L., Ma, S., Obst, U. & Rebek, J. Jr (1999). *J. Am. Chem. Soc.* **121**, 7973–7974.