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1-(4-Chlorophenacyl)-2-methyl-4,5-dinitro-1*H*-imidazole

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In the title compound, $C_{12}H_9ClN_4O_5$, both nitro groups are rotated significantly from the imidazole plane. The C-4—NO_2 bond length is only slightly shorter than the value for a normal single Csp^2—NO_2 bond and the C-5—NO_2 bond length is significantly shorter than C-4—NO_2. In consequence, the C-4-nitro group is easily replaced by morpholine, while the C-5-nitro group shows an extraordinary stability on treatment with the amine. In the crystal structure, the molecules are linked through C—H···O hydrogen bonds.

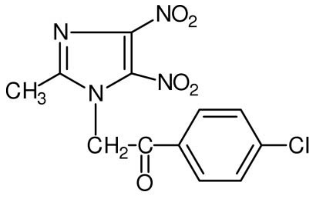
Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.002 Å
R factor = 0.038
wR factor = 0.117
Data-to-parameter ratio = 13.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

1-(4-Chlorophenacyl)-2-methyl-4,5-dinitroimidazole, (I), has been used as a substrate in nucleophilic substitution with morpholine. The only product isolated from the reaction mixture was 1-(4-chlorophenacyl)-2-methyl-4-morpholino-5-nitroimidazole, even when the amine was used in sixfold excess at elevated reaction temperature (Zaprutko *et al.*, 1989). In order to explain the behaviour of the nitro groups in the reaction with morpholine, compound (I) was subjected to an X-ray crystallographic study.



(I)

Results of the X-ray analysis show that the C4- and C5-nitro groups subtend different interplanar angles of 46.16 (10) and 14.9 (3)°, respectively, to the imidazole ring. Some differences are also noted in the exocyclic C—NO_2 bond distances. The C4—N16 distance of 1.445 (2) Å is longer than the C5—N19 bond of 1.424 (2) Å by about 7*σ*. The former is only slightly shortened with respect to the normal length of the Csp^2—NO_2 bond of 1.468 (1) Å (Allen *et al.*, 1987). This observation indicates weak conjugation between the C5-nitro group and the imidazole ring, despite the rotation of this substituent from the five-membered heterocyclic ring plane by about 15°. The dihedral angles between the nitro groups and the imidazole ring observed in compound (I) have also been noted in 3-chloro-1-(4,5-dinitroimidazol-1-yl)propan-2-ol (Gzella *et al.*, 1999) [C4—NO_2 = 20.3 (2)° and C5—NO_2 = 42.8 (1)°]. In spite of that, the lengths of the bonds C—NO_2 in the two nitro groups are comparable [C4—NO_2 = 1.442 (3) Å and C5—NO_2 = 1.448 (4) Å] and are similar to the C4—N16 bond distance of (I). It should be emphasized that in 3-chloro-1-

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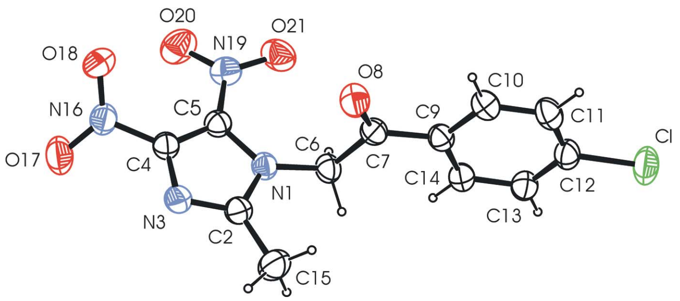

Figure 1
The molecular structure of (I), showing the atomic labelling scheme. Non-H atoms are drawn as 30% probability displacement ellipsoids.

(4,5-dinitroimidazol-1-yl)propan-2-ol, both nitro groups are exchanged for a morpholine residue. As follows from the above discussion, the inability of the C5-nitro group in compound (I) to undergo nucleophilic substitution is mainly a result of the shortening of the C—NO_2 bond and, to a lower degree, its orientation.

The C6/C7/O8/C9 fragment of the chlorophenacyl substituent is flat and approximately perpendicular to the imidazole ring [dihedral angle = 84.83 (6)°]. The phenyl ring is twisted by 5.69 (13)° from the C6/C7/O8/C9 plane and makes a dihedral angle of 83.44 (5)° with the imidazole ring. This mutual arrangement of these systems is frequently observed in other phenacyl derivatives of imidazole (Borowiak *et al.*, 1989; Wolska *et al.*, 1991, 1993, 1994; Zaprutko *et al.*, 2003). The group C7═O8 belonging to the phenacyl system assumes a synperiplanar conformation with respect to the N1—C6 bond [N1—C6—C7—O8 = 5.5 (2)°].

In the crystal structure of (I), the molecules are connected by C—H···O hydrogen bonds, forming a two-dimensional hydrogen-bond network parallel to the *bc* plane (Table 1 and Fig. 2).

Experimental

Compound (I) was synthesized according to the literature procedure of Zaprutko *et al.*, (1989). Crystals suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of a methanol solution.

Crystal data

$C_{12}H_9ClN_4O_5$
$M_r = 324.68$
Monoclinic, $C2/c$
$a = 20.094\ (3)$ Å
$b = 9.4907\ (14)$ Å
$c = 15.0418\ (17)$ Å
$\beta = 106.953\ (12)°$
$V = 2743.9\ (7)$ Å^3
$Z = 8$
$D_x = 1.572$ Mg m^{-3}
Cu $K\alpha$ radiation
$\mu = 2.78$ mm^{-1}
$T = 293\ (2)$ K
Prism, yellow
0.60 × 0.30 × 0.28 mm

Data collection

Kuma KM-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan
  (North *et al.*, 1968)
  $T_{min} = 0.203$, $T_{max} = 0.459$
5181 measured reflections
2615 independent reflections
2316 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 70.1°$
2 standard reflections
  every 100 reflections
  intensity decay: <2%

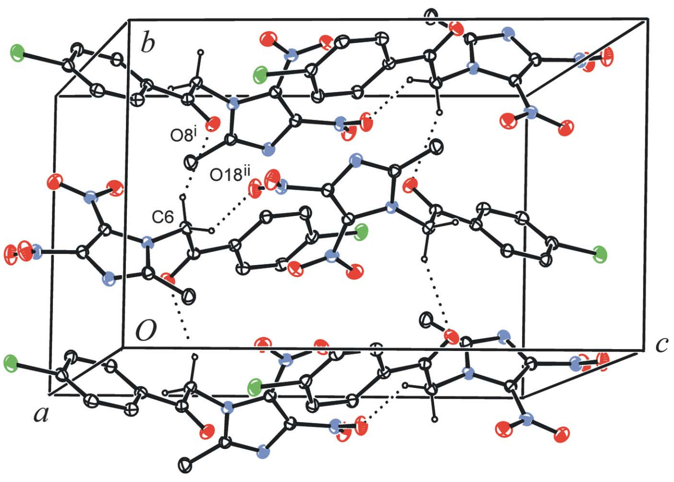

Figure 2
The hydrogen bonding (dotted lines) in (I) [symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $x, 1 - y, \frac{1}{2} - z$]. H atoms not involved in hydrogen bonds have been omitted for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.117$
$S = 1.03$
2615 reflections
200 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.8575P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6*B*···O21	0.97	2.34	2.803 (2)	108
C6—H6*B*···O8^{i}	0.97	2.54	3.427 (2)	152
C6—H6*A*···O18^{ii}	0.97	2.37	3.178 (2)	140

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

All H atoms were placed in geometrically calculated positions and were refined using a riding model, with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl H atoms. The methyl group was refined as a rigid group, which was allowed to rotate.

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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