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N,*N*-Dimethyl-5-[2-(hydroxymethyl)-4-nitrophenyl]pent-4-ynamide

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Key indicators

Single-crystal X-ray study
T = 161 K
Mean σ(C–C) = 0.003 Å
R factor = 0.054
wR factor = 0.149
Data-to-parameter ratio = 19.6

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

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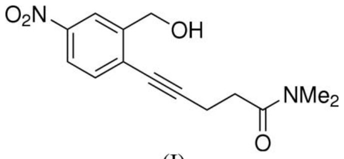
Molecules of title title compound, $C_{14}H_{16}N_2O_4$, crystallize as centrosymmetric dimers, connected by intermolecular O—H···O hydrogen bonds.

Comment

The title compound, (I), was prepared for an investigation of the addition of nucleophiles to C≡C triple bonds and the C—H activation in the benzylic position by homogeneous gold catalysts (Hashmi, 2004).



(I)

The angle between the planes of the benzene ring and the nitro group is 3.9 (1)°. The C7—O3 bond is almost coplanar with the benzene ring. This conformation results in a contact distance of 2.33 Å between atoms O3 and H6. The amide group is approximately planar. The amide N atom shows no deviation from planarity; the sum of the three valence angles about atom N2 is 360.0°. The molecules form centrosymmetric dimers connected by intermolecular O—H···O hydrogen bonds. The structure of the dimer is shown in Fig. 1 and details

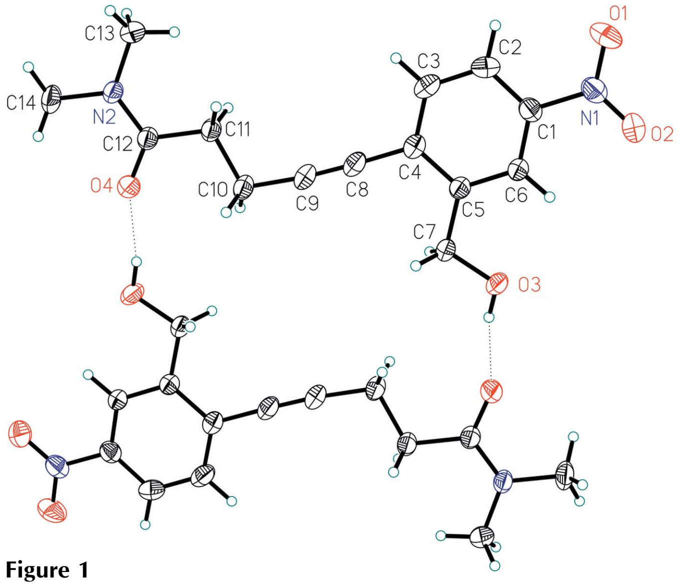


Figure 1
The structure of a centrosymmetric dimer of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radius and hydrogen bonds are shown as dotted lines.

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of the hydrogen bonding are given in Table 2. The hydrogen-bond formation results in an approximate coplanarity of the benzene group and the amide group; the angle between the benzene ring and the plane of the *N*,*N*-dimethylamide group is 8.0 (1)°. A very different conformation has been observed for the corresponding molecule without a nitro group attached to the benzene ring (Bats *et al.*, 2006). Those molecules are arranged in hydrogen-bonded chains, and the angles between the benzene plane and the plane of the *N*,*N*-dimethylamide group range from 74.6 (1) to 82.2 (1)°.

The crystal packing is shown in Fig. 2. Neighboring dimers are connected by three different, very weak intermolecular C—H···O interactions, with H···O distances of 2.59, 2.66 and 2.66 Å and O—H···O angles of 144, 160 and 109°. There is also a weak intermolecular C(methyl)—H···π(alkyne) contact, with an H···*Cg* distance of 2.83 Å and a C—H···*Cg*$^{\rm ii}$ angle of 142° [*Cg* is the mid-point of the C≡C triple bond; symmetry code: (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$].

Experimental

The title compound was prepared using the Sonogashira coupling of 2-bromo-(5-nitrophenyl)methanol and *N*,*N*-dimethylpent-4-ynamide (Thorand & Krause, 1998). Single crystals were obtained by evaporation of a solution of (I) in methanol/ethyl acetate (1/1 *v*/*v*).

Crystal data

$C_{14}H_{16}N_2O_4$
$M_r = 276.29$
Monoclinic, $P2_1/c$
$a = 12.877$ (3) Å
$b = 14.3165$ (18) Å
$c = 7.5960$ (15) Å
$\beta = 102.934$ (8)°
$V = 1364.8$ (5) Å^3
$Z = 4$

$D_x = 1.345$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 119 reflections
$\theta = 3$–23°
$\mu = 0.10$ mm^{-1}
$T = 161$ (2) K
Block, yellow
0.26 × 0.24 × 0.18 mm

Data collection

Siemens SMART 1K CCD diffractometer
ω scans
Absorption correction: none
21386 measured reflections
3663 independent reflections

2205 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.055$
$\theta_{\rm max} = 29.5°$
$h = -17 \rightarrow 17$
$k = -19 \rightarrow 19$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.149$
$S = 1.03$
3663 reflections
187 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.6P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}

Table 1
Selected torsion angles (°).

C6—C5—C7—O3	6.3 (3)	C13—N2—C12—O4	−176.00 (18)

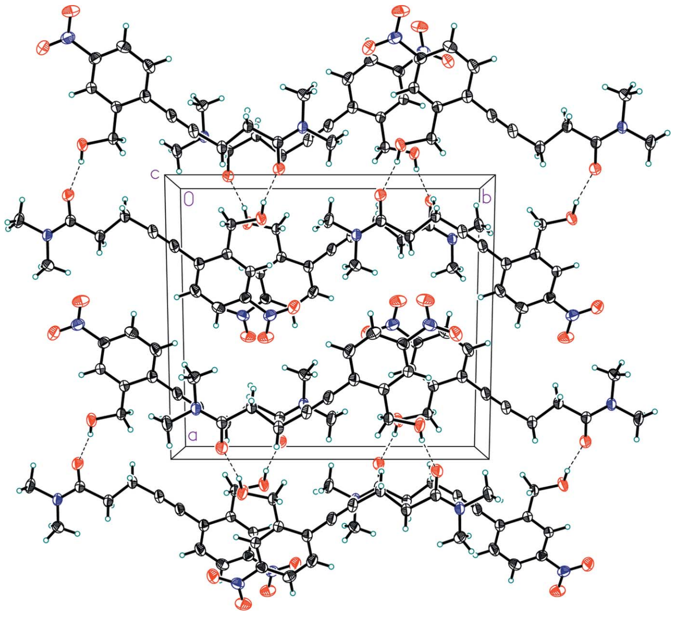

Figure 2
The crystal packing of (I), viewed down c. Displacement ellipsoids are drawn at the 50% probability level and hydrogen bonds are shown as broken lines.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*B*···O4$^{\rm i}$	0.88 (3)	1.85 (3)	2.712 (2)	164 (2)

Symmetry code: (i) $-x+2, -y+1, -z$.

H atoms attached to C atoms were positioned geometrically and refined as riding atoms [Csp^2—H = 0.95 Å and secondary C—H = 0.99 Å, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C), and methyl C—H = 0.98 Å with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C)]. The hydroxyl H atom was located in a difference Fourier map and was refined isotropically.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL97*.

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