Crystal structure of 2-(adamantan-1-yl)-5-(3,5-dinitrophenyl)-1,3,4-oxadiazole, C18H18N4O5

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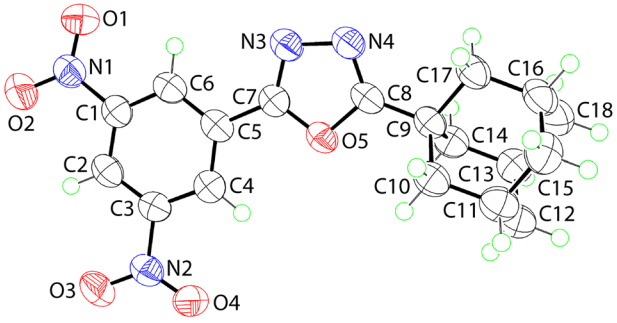

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Abstract

$C_{18}H_{18}N_4O_5$, monoclinic, $P2_1/c$ (no. 14), a = 11.7553(8) Å, b = 6.4876(4) Å, c = 22.3442(15) Å, β = 91.263(7)°, V = 1703.64(19) Å^3, Z = 4, $R_{gt}(F)$ = 0.0531, $wR_{ref}(F^2)$ = 0.1376, T = 160 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless plate
Size:	0.12 × 0.07 × 0.01 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	0.90 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	74.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6232, 6232
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 4033
$N(param)_{refined}$:	245
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

A mixture of adamantane-1-carboxylic acid (1.8 g, 0.01 mol), 3,5-dinitrobenzoyl chloride (2.3 g, 0.01 mol) and phosphorus oxychloride (8 mL) was heated under reflux for 1 h. On cooling, crushed ice (50 g) was added cautiously and the mixture stirred for 30 min. The precipitated crude product was filtered, washed with saturated sodium hydrogen carbonate solution and finally with water, dried and crystallised from ethanol to yield 3.41 g (92%) of the title compound (I) as colourless plates. M.pt.: 473–475 K (uncorrected). **Anal. Calcd.** for $C_{18}H_{18}N_4O_5$: C, 58.37; H, 4.90; N, 15.13%. Found: C, 58.33; H, 4.92; N, 15.09%. **^{1}H NMR** (DMSO-d6, 700.17 MHz): δ 1.80–1.82 (m, 6H, Adamantane–H), 2.01–2.13 (m, 9H, Adamantane–H), 8.99 (s, 1H, Ar–H), 9.02 (s, 2H, Ar–H). **^{13}C{^{1}H} NMR** (DMSO-d6, 176.08 MHz): δ 27.61, 34.53, 36.12, 39.63 (Adamantane–C), 121.34, 126.82, 126.86, 149.21 (Ar–C), 161.55, 173.81 (Oxadiazole–C). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of (I) in EtOH/$CHCl_3$ (1:1) at room temperature.

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The crystal was refined as a twin with a 180° rotation about [0 0 1]; the major component of the twin was refined to 0.5597(14).

Comment

Adamantane-containing derivatives were recognized early for their diverse chemotherapeutic properties and several adamantane derivatives are currently used in efficient therapies as anti-viral, anti-cancer and anti-microbial

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8577 (2)	0.7819 (4)	0.69232 (10)	0.0333 (6)
C2	0.8024 (2)	0.9481 (4)	0.71731 (10)	0.0353 (6)
H2	0.842743	1.053385	0.738362	0.042*
C3	0.6859 (2)	0.9527 (4)	0.71004 (10)	0.0323 (5)
C4	0.6242 (2)	0.8020 (4)	0.68018 (10)	0.0324 (5)
H4	0.543881	0.812750	0.675324	0.039*
C5	0.6827 (2)	0.6341 (4)	0.65740 (10)	0.0325 (6)
C6	0.8009 (2)	0.6237 (4)	0.66345 (10)	0.0340 (6)
H6	0.841465	0.509658	0.647932	0.041*
C7	0.6221 (2)	0.4643 (4)	0.62800 (10)	0.0317 (5)
C8	0.4828 (2)	0.2888 (4)	0.59284 (10)	0.0330 (6)
C9	0.3623 (2)	0.2453 (4)	0.57540 (11)	0.0328 (6)
C10	0.2827 (2)	0.2846 (5)	0.62800 (11)	0.0385 (6)
H10A	0.304942	0.195270	0.662224	0.046*
H10B	0.289245	0.430014	0.641056	0.046*
C11	0.1596 (3)	0.2382 (5)	0.60835 (12)	0.0418 (6)
H11	0.108048	0.262139	0.642671	0.050*
C12	0.1254 (3)	0.3810 (5)	0.55639 (12)	0.0422 (6)
H12A	0.045432	0.353884	0.543939	0.051*
H12B	0.131343	0.526470	0.569435	0.051*
C13	0.2035 (3)	0.3437 (5)	0.50361 (11)	0.0392 (6)
H13	0.180847	0.436678	0.469698	0.047*
C14	0.3271 (2)	0.3877 (4)	0.52273 (11)	0.0371 (6)
H14A	0.334896	0.533664	0.535099	0.045*
H14B	0.377670	0.363704	0.488570	0.045*
C15	0.1504 (3)	0.0140 (5)	0.58816 (13)	0.0456 (7)
H15A	0.172820	−0.078254	0.621692	0.055*
H15B	0.070632	−0.017583	0.576332	0.055*
C16	0.2277 (3)	−0.0235 (5)	0.53526 (12)	0.0424 (6)
H16	0.220315	−0.170242	0.521993	0.051*
C17	0.3513 (3)	0.0192 (4)	0.55500 (12)	0.0381 (6)
H17A	0.402608	−0.006822	0.521266	0.046*
H17B	0.373608	−0.073891	0.588344	0.046*
C18	0.1941 (3)	0.1192 (5)	0.48338 (12)	0.0434 (7)
H18A	0.244738	0.094967	0.449281	0.052*
H18B	0.114952	0.089406	0.469918	0.052*
N1	0.9822 (2)	0.7726 (4)	0.69664 (9)	0.0386 (5)
N2	0.6232 (2)	1.1268 (4)	0.73577 (9)	0.0366 (5)
N3	0.6651 (2)	0.2948 (4)	0.60817 (9)	0.0364 (5)
N4	0.5728 (2)	0.1799 (4)	0.58514 (9)	0.0361 (5)
O1	1.03085 (17)	0.6403 (3)	0.66813 (8)	0.0434 (5)
O2	1.0322 (2)	0.8980 (4)	0.72841 (11)	0.0627 (7)
O3	0.6754 (2)	1.2451 (4)	0.76899 (10)	0.0551 (6)
O4	0.52210 (17)	1.1428 (3)	0.72273 (8)	0.0429 (5)
O5	0.50776 (16)	0.4750 (3)	0.62007 (7)	0.0334 (4)

agents [5, 6]. On the other hand, the 1,3,4-oxadiazole heterocycle represents the core pharmacophore of several marketed drugs [7, 8]. In the present study, the crystal structure of an adamantane-1,3,4-oxadiazole hybrid molecule, (I), is described and its features compared to literature precedents [9–14].

The molecular structure of (I) is shown in Figure (50% probability ellipsoids). The molecule comprises a central 1,3,4-oxadiazole ring connected at the C1-position to an adamantan-1-yl residue and at the C2-position to a 3,5-dinitrophenyl ring. Within the ring, the C7–N3 [1.292(4) Å] and C8–N4 [1.287(4) Å] bond lengths are consistent with substantial double-bond character with the N3–N4 bond length being 1.405(3) Å. The small elongation and shortening of the C–N and N–N bonds from their standard values is indicative of delocalisation of π-electron density in the ring; the r.m.s. deviation of the five atoms comprising the ring is 0.002 Å, consistent with strict planarity. The substituted phenyl ring forms a dihedral angle of 4.73(13)° with the five-membered ring. The N1- and N2-nitro groups are twisted out of the phenyl ring they are connected to, as seen in the dihedral angles between the respective least-squares planes of 9.38(12)° and 9.94(16)°. The dihedral angle between the nitro substituents [10.3(3)°] is indicative of a conrotatory relationship.

There are five literature precedents for (I) which differ only in the nature of the phenyl-bound substituents. These are the 4-fluoro [9], 4-chloro [9], 4-bromo [10], 4-nitro [11] and 3-fluoro [12] derivatives. The molecules adopt approximately the same conformations to that seen in (I) but with a range of nearly 21° in the dihedral angles formed between the five- and six-membered rings. Thus, for the 4-substituted molecules, the dihedral angles are 20.79(15)°, 9.48(7)°, 10.41(5)° and 0° [the molecule is bisected by a mirror plane], respectively. For the two independent molecules comprising the asymmetric-unit of the 3-fluoro species, the independent dihedral angles are 3.0(3)° and 3.3(3)°. Two other molecules worthy of mention are those where the adamantan-1-yl residue of (I) is substituted by a second 3,5-dinitrophenyl substituent [13] and a 2-(4-chlorophenyl)-1*H*-1,3-benzodiazole [14]. The bond lengths in the 1,3,4-oxadiazole ring of both structures match those noted for (I).

In the molecular packing of (I), helical chains along the 2_1-screw axis along the b-direction feature phenyl–C–H···O(nitro) contacts [C2–H2···O1^{i}: H6···O2^{i} = 2.60 Å, C6···O2^{i} = 3.425(3) Å with angle at H6 = 146° for symmetry operation i: $2 - x$, $1/2 + y$, $3/2 - z$]. Within the individual stacks comprising the chain, there are additional nitro-O···π(oxadiazole) interactions whereby the nitro-group is approximately parallel to a translationally related five-membered ring, forming a dihedral angle of 12.2(2)° [O4···Cg(oxadiazole)^{ii} = 2.955(2) Å with angle at O4 = 92.42(14)° for ii: x, $-1 + y$, z]. Centrosymmetrically related helical chains are connected into a double layer by methylene–C—H···π(oxadiazole) interactions [C14–H14b···Cg(oxadiazole)^{iii} = 2.94° with angle at H10 = 126° for

iii: 1 – x, 1 – y, 1 – z]. The layers stack along the c-axis without directional interactions between them.

Given all of the specified interactions identified from a geometric-based analysis of the molecular packing are relatively weak. It was thought worthwhile to conduct a complimentary analysis of the calculated Hirshfeld surfaces, encompassing the full and decomposed two-dimensional fingerprint plots, employing Crystal Explorer 17.5 [15] and following established procedures [16]. Despite their being only one H···O contact less than the sum of the van der Waals radii, O···H/H···O contacts make up 30.3% of all surface contacts. This contribution is only exceeded by H···H contacts at 33.4%. The next two most important percentage contributions come from N···H/H···N [11.5%] and C···H/H···C [10.1%] contacts. The next two significant surface contacts are O···C/C···O [5.0%] and O···O [4.2%]. The remaining contacts are due to N···C/C···N [2.5%], O···N/N···O [2.2%] and N···N [0.9%].

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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