

Acta Crystallographica Section C

**Crystal Structure  
Communications**

ISSN 0108-2701

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## *N*-(4-Methylphenyl)-*N*-(5-nitro-furfuryl)-*N*-prop-2-ynylamine

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Received 25 August 2000

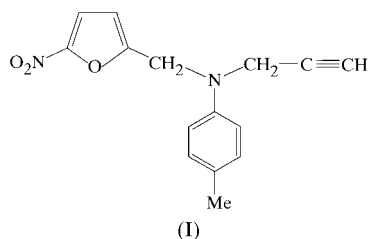
Accepted 21 September 2000

Data validation number: IUC0000267

The title compound, C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>, is the first example of a structurally determined tertiary amine with both *N*-5-nitrofurfuryl and *N*-prop-2-ynyl moieties. The molecule is not planar, *i.e.* the furan ring is inclined at an angle of 84.35 (4)° to the phenyl ring. The crystal structure is dominated by van der Waals forces. The terminal alkynyl group as the strongest C—H hydrogen-bond donor is not involved in hydrogen-bond formation.

### Comment

As part of continuing efforts (Mance *et al.*, 1997) to study the intramolecular Diels–Alder reaction of tertiary *N*-alkenyl-furfurylamine (Klepo & Jakopčić, 1987; Mance *et al.*, 1996), we find it necessary to prepare the corresponding *N*-prop-2-ynyl derivatives and compare the dienophylic capability of the alkynyl and alkenyl moieties in an IMDAF reaction (intramolecular Diels–Alder reaction of furan compounds). Besides the potential biological activity (Simon *et al.*, 1986, 1998) of the title compound, (I), the norbornane-like product of the IMDAF reaction would be useful in our intended photochemical studies.



In the title compound, the furan and phenyl rings are almost perpendicular. The dihedral angle calculated through the ring

atoms is 84.35 (4)°. The bond distances within the furan ring and *p*-tolyl moiety are normal (Allen *et al.*, 1987). Two furan bonds are shorter [C2—C3 1.356 (2) and C4—C5 1.341 (2) Å], while the C3—C4 bond distance is 1.416 (2) Å [according to the Cambridge Structural Database (Allen & Kennard, 1993), the corresponding mean bond distance values for 57 5-nitrofuran structural fragments are 1.360 (4), 1.346 (2) and 1.409 (2) Å, respectively]. The slight discrepancy of the C—O bond values within the furan ring [O1—C2 1.375 (2) and O1—C5 1.356 (2) Å] depends on the electronic properties of the NO<sub>2</sub> and methylene CH<sub>2</sub> groups, which substitute the furan ring at positions 2 and 5, respectively. Two C—N distances [N1—C1 1.443 (2) and N1—C13 1.458 (2) Å] correspond to single C—N bond-length values, while the N1—C6 bond of 1.396 (2) Å is shorter as a result of  $\pi$ -electron delocalization. The sum of the angles around the amine N atom is in accord with  $sp^2$  hybridization. The C≡C bond value in the propynyl moiety [C14≡C15 1.183 (2) Å] is in agreement with the average value found for the X—C≡C—X fragment (1.183 Å, X is any atom; Allen *et al.*, 1987). The furan ring is planar, with O1 displaced from the best plane formed by the other ring atoms by −0.005 (1) Å. The molecules are linked together by van der Waals forces only. The alkynyl acid proton does not participate in hydrogen-bond formation, as established by the X-ray single-crystal diffractometry and spectroscopic analysis (Calabrese *et al.*, 1970; Steiner, 1995; Steiner *et al.*, 1997).

### Experimental

Treating the secondary amine (0.46 g, 2 mmol) with a slight excess of prop-2-ynyl bromide under stirring and cooling in a nitrogen atmosphere, gave, after neutralization with 5% aqueous sodium hydroxide and extraction with ether, the tertiary amine in a good yield (0.52 g, 94%; m.p. 357–358 K) and was identified by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  3280 (H—C≡C); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta/\text{p.p.m.}$ : 7.24 (*d*, 1H, *J* = 3.7 Hz) and 6.45 (*d*, 1H, *J* = 3.7 Hz) for furan H-4 and H-3 protons; 7.09 (*d*, 2H, *J* = 8.5 Hz) and 6.82 (*d*, 2H, *J* = 8.5 Hz) for *p*-phenylene CH; 4.56 (*s*, 2H) for 2-furfuryl CH<sub>2</sub> and 4.06 (*s*, 2H) for propargyl CH<sub>2</sub> protons; 2.27 (*s*, 3H) for *p*-phenylene CH<sub>3</sub>; 2.25 (*s*, 1H) for propargyl —CH; <sup>13</sup>C NMR (CDCl<sub>3</sub>)/*p.p.m.*: 156.4 (*s*), 151.4 (*s*), 112.5 (*d*) and 111.0 (*d*) for furan C atoms; 145.0 (*s*), 129.1 (*s*), 129.7 (*d*) and 115.1 (*d*) for *p*-phenylene C atoms; 98.8 (*s*), 73.0 (*d*) and 41.0 (*t*) for propargyl; 48.8 (*t*) for 2-furyl CH<sub>2</sub> and 20.2 (*q*) for *p*-phenylene CH<sub>3</sub>. Purification by column chromatography on neutral aluminium oxide and recrystallization from ethanol yielded pale-orange crystals of good diffraction quality.

### Crystal data

C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>

*M<sub>r</sub>* = 270.28

Triclinic, *P* $\bar{1}$

*a* = 8.8490 (18) Å

*b* = 9.2060 (13) Å

*c* = 9.8438 (19) Å

$\alpha$  = 63.196 (14)°

$\beta$  = 76.908 (15)°

$\gamma$  = 73.937 (13)°

*V* = 683.0 (2) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.314 Mg m<sup>−3</sup>

Mo *K* $\alpha$  radiation

Cell parameters from 57 reflections

$\theta$  = 8–17.8°

$\mu$  = 0.093 mm<sup>−1</sup>

*T* = 293 (2) K

Prism, pale orange

0.690 × 0.450 × 0.135 mm

Data collection

Philips PW1100 updated by Stoe diffractometer  
 $\omega$  scans  
 7040 measured reflections  
 3520 independent reflections  
 1997 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.105$

$\theta_{\text{max}} = 29.02^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -12 \rightarrow 12$   
 $l = -13 \rightarrow 13$   
 5 standard reflections  
 frequency: 90 min  
 intensity decay: 7.2%

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.101$   
 $S = 0.973$   
 3520 reflections  
 186 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0189P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.17 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.16 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

N1—C6	1.3956 (14)	C13—C14	1.4737 (18)
N1—C1	1.4432 (16)	C14—C15	1.183 (2)
N1—C13	1.4584 (16)		
C13—C14—C15	177.26 (15)		

H atoms were placed in geometrically calculated positions and constrained to ride on their parent C atoms with C—H distances of 0.93  $\text{\AA}$  for  $\text{Csp}^2$  atoms, 0.96  $\text{\AA}$  for methyl and 0.97  $\text{\AA}$  for methylene groups, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  or  $1.5U_{\text{eq}}$  (for methyl groups) of the carrier C atoms. The propynyl H atom was found in a difference synthesis and was refined isotropically; C15—H15 1.02 (2)  $\text{\AA}$  and C14—C15—H15 angle 177.6 (15)  $^\circ$ .

Data collection: *STAD14* (Stoe & Cie, 1995); cell refinement: *STAD14*; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

This research was supported by the Ministry of Science and Technology of the Republic of Croatia (grant No. 125004).

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