Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-(4-Ethynylphenyl)-3,5-dimethylbiuret

William T. A. Harrison

Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: w.harrison@abdn.ac.uk

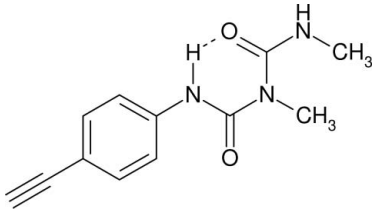
Received 17 August 2007; accepted 18 August 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.037; wR factor = 0.105; data-to-parameter ratio = 13.4.

In the title compound, $C_{12}H_{13}N_3O_2$, an intramolecular N—H···O bond helps to establish the near-planar conformation; the two –NH–CO–N– fragments of the biuret backbone are twisted by 4.96 (10)°. An acute intermolecular N—H···O hydrogen bond helps to define the crystal packing.

Related literature

For related structures, see: Ahmed *et al.* (1972); Craven (1973); Carugo *et al.* (1992); Deschamps *et al.* (1998). For geometric analysis, see Spek (2003).



Experimental

Crystal data

$C_{12}H_{13}N_3O_2$
M_r = 231.25
Monoclinic, $P2_1/n$
a = 6.7870 (5) Å
b = 11.1876 (8) Å
c = 15.8669 (11) Å
β = 97.180 (2)°
V = 1195.33 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 (2) K
0.36 × 0.30 × 0.20 mm

Data collection

Bruker SMART1000 CCD diffractometer
Absorption correction: none
6817 measured reflections
2101 independent reflections
1465 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.105
S = 0.98
2101 reflections
157 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.11 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.86	1.82	2.5451 (17)	141
N3—H3···O1^{i}	0.86	2.20	2.9245 (17)	141

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The author thanks Stuart Aiken and M. John Plater for supplying the sample.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2190).

References

Ahmed, N. A., Kitaigorodsky, A. I. & Sirota, M. I. (1972). *Acta Cryst.* B**28**, 2875–2877.
Bruker (1999). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Carugo, O., Poli, G. & Manzoni, L. (1992). *Acta Cryst.* C**48**, 2013–2016.
Craven, B. M. (1973). *Acta Cryst.* B**29**, 1525–1528.
Deschamps, J. R., George, C., Flippen-Anderson, J. L., DeMilo, A. B. & Bordas, B. (1998). *J. Chem. Crystallogr.* **28**, 453–459.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

 doi:10.1107/S1600536807040895

supplementary materials

Acta Cryst. (2007). E**63**, o3883 [**doi:10.1107/S1600536807040895**]

1-(4-Ethynylphenyl)-3,5-dimethylbiuret

W. T. A. Harrison

Comment

The title compound, (I), was prepared as an intermediate in the synthesis of new multidentate porphyrin-like ligands.

On progressing along the chain formed by atoms N1, C9, N2, C11, and N3 (Fig. 1), the C–N bond lengths in (I) show a short-long-long-short pattern, although all of them are intermediate between typical C–N single (1.47 Å) and C=N double (1.30 Å) bonds. Bond-angle sums about the three N atoms in (I) yielded values of 360.0° in each case suggesting that all these species can be regarded as being sp^2 hybridized, indicating a significant degree of electronic delocalization over the entire biuret fragment (Carugo *et al.*, 1992).

Similar variations in C–N bond-lengths to those of (I) were seen in biuret monohydrate (Craven, 1973), although other biurets show a distinctly different pattern, such as the monoclinic polymorph of 1-(2,6-difluorobenzoyl)-5-(4-chlorophenyl)biuret (Deschamps *et al.*, 1998) in which a short-long-short-long sequence [C–N = 1.344 (4), 1.412 (4), 1.352 (4) and 1.407 (4) Å] occurs.

The two –NH—CO—N– fragments making up the biuret unit in (I) are planar within experimental error. The dihedral angle between these two groupings is 4.96 (10)°, which is at the lower end of the range of this parameter observed in related compounds (Carugo *et al.*, 1992).

The ethynylphenyl moiety (atoms C1—C8) in (I) is twisted by 11.23 (7)° with respect to the N1/C9/O1/N2, grouping, although the C6—N1 bond [1.4026 (19) Å] appears to have significant double bond character. A *PLATON* analysis (Spek, 2003) of (I) suggested that the C2—C3 bond is unusually long [1.443 (2) Å] for a C(*sp*)—C(sp^2) contact. However, a similar bond length (1.445 Å; s.u. not stated) has been seen for the equivalent bond in 1,4-diethynylbenzene (Ahmed *et al.*, 1972).

A bent, intramolecular, N1—H1···O2 bond is present in (I) (Table 1), with the component atoms making up a six-ring loop, this being a common motif in biurets (Carugo *et al.*, 1992).

In the crystal of (I), the molecules are linked into infinite chains which propagate in [010] by way of the N3—H3···O1^{i} bond (see Table 1). There are no significant π-π, C—H···O or C—H···π interactions in (I).

Experimental

The title compound was prepared by reacting 1-(4-ethynylphenyl)biuret with MeI in THF (Aiken & Plater, 2007, unpublished work).

Refinement

The H atoms were placed geometrically (N—H = 0.86 Å; C—H = 0.93–0.96 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(carrier) or 1.5U_{eq}(methyl C). The methyl group was allowed to rotate, but not to tip, to best fit the electron density.

Figures

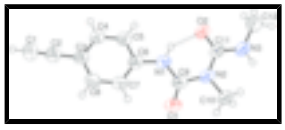


Fig. 1. The molecular structure of (I) (50% displacement ellipsoids, arbitrary spheres for the H atoms, hydrogen bond indicated by a double dashed line).

1-(4-Ethynylphenyl)-3,5-dimethylbiuret

Crystal data

$C_{12}H_{13}N_3O_2$	F_{000} = 488
M_r = 231.25	D_x = 1.285 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 2287 reflections
a = 6.7870 (5) Å	θ = 2.2–25.0º
b = 11.1876 (8) Å	μ = 0.09 mm^{-1}
c = 15.8669 (11) Å	T = 293 (2) K
β = 97.180 (2)º	Block, colourless
V = 1195.33 (15) Å^3	0.36 × 0.30 × 0.20 mm
Z = 4	

Data collection

Bruker SMART1000 CCD diffractometer	1465 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.024
Monochromator: graphite	θ_{max} = 25.0º
T = 293(2) K	θ_{min} = 2.2º
ω scans	h = −6→8
Absorption correction: none	k = −12→13
6817 measured reflections	l = −18→18
2101 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.037	$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2]$

	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.105$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.98$	$\Delta\rho_{max} = 0.15$ e Å^{-3}
2101 reflections	$\Delta\rho_{min} = -0.11$ e Å^{-3}
157 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.016 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.24431 (16)	0.54995 (11)	0.34396 (7)	0.0731 (4)
O2	0.71481 (14)	0.32197 (11)	0.35264 (7)	0.0689 (4)
N1	0.56872 (18)	0.51965 (11)	0.39439 (8)	0.0569 (4)
H1	0.6618	0.4672	0.3961	0.068*
N2	0.38323 (17)	0.37021 (12)	0.31831 (7)	0.0527 (3)
N3	0.51702 (19)	0.19015 (13)	0.27910 (9)	0.0709 (4)
H3	0.4021	0.1736	0.2524	0.085*
C1	0.8880 (3)	1.02491 (19)	0.60840 (13)	0.0836 (6)
H1A	0.9375	1.0915	0.6391	0.100*
C2	0.8256 (3)	0.94085 (17)	0.56966 (10)	0.0660 (5)
C3	0.7550 (2)	0.83572 (14)	0.52261 (10)	0.0577 (4)
C4	0.8886 (2)	0.74785 (15)	0.50449 (10)	0.0643 (5)
H4	1.0236	0.7579	0.5218	0.077*
C5	0.8221 (2)	0.64615 (15)	0.46107 (10)	0.0619 (4)
H5	0.9131	0.5885	0.4489	0.074*
C6	0.6211 (2)	0.62841 (14)	0.43513 (9)	0.0523 (4)
C7	0.4871 (2)	0.71615 (15)	0.45250 (10)	0.0588 (4)
H7	0.3521	0.7063	0.4351	0.071*
C8	0.5556 (2)	0.81836 (15)	0.49591 (10)	0.0617 (4)
H8	0.4650	0.8767	0.5074	0.074*
C9	0.3921 (2)	0.48661 (15)	0.35301 (9)	0.0528 (4)
C10	0.1859 (2)	0.32878 (16)	0.28153 (10)	0.0676 (5)
H10A	0.0862	0.3805	0.2995	0.101*
H10B	0.1651	0.2487	0.3003	0.101*

H10C	0.1772	0.3300	0.2207	0.101*
C11	0.5479 (2)	0.29428 (15)	0.31843 (9)	0.0535 (4)
C12	0.6776 (3)	0.1042 (2)	0.28120 (15)	0.0998 (7)
H12A	0.6411	0.0422	0.2404	0.150*
H12B	0.7028	0.0698	0.3369	0.150*
H12C	0.7953	0.1436	0.2677	0.150*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0518 (7)	0.0721 (8)	0.0894 (9)	0.0121 (6)	−0.0144 (6)	0.0026 (6)
O2	0.0386 (6)	0.0772 (8)	0.0882 (8)	−0.0008 (5)	−0.0033 (5)	−0.0225 (6)
N1	0.0416 (7)	0.0594 (8)	0.0672 (8)	0.0029 (6)	−0.0024 (6)	−0.0024 (6)
N2	0.0377 (7)	0.0630 (8)	0.0552 (7)	−0.0028 (5)	−0.0020 (5)	0.0025 (6)
N3	0.0439 (8)	0.0824 (10)	0.0832 (10)	−0.0021 (7)	−0.0045 (7)	−0.0281 (8)
C1	0.0899 (15)	0.0771 (14)	0.0814 (13)	0.0077 (11)	0.0013 (10)	−0.0222 (11)
C2	0.0683 (11)	0.0668 (12)	0.0612 (10)	0.0097 (9)	0.0014 (8)	−0.0029 (9)
C3	0.0613 (11)	0.0577 (10)	0.0525 (8)	0.0066 (8)	0.0013 (7)	0.0027 (8)
C4	0.0501 (10)	0.0674 (11)	0.0724 (10)	0.0016 (8)	−0.0040 (8)	−0.0068 (9)
C5	0.0473 (10)	0.0647 (11)	0.0716 (10)	0.0090 (7)	−0.0009 (7)	−0.0074 (8)
C6	0.0484 (9)	0.0567 (10)	0.0507 (8)	0.0004 (7)	0.0016 (7)	0.0057 (7)
C7	0.0466 (9)	0.0670 (11)	0.0616 (10)	0.0075 (7)	0.0015 (7)	0.0043 (8)
C8	0.0596 (11)	0.0625 (11)	0.0627 (10)	0.0137 (8)	0.0064 (8)	0.0018 (8)
C9	0.0448 (9)	0.0625 (11)	0.0498 (8)	0.0004 (7)	0.0014 (7)	0.0092 (7)
C10	0.0412 (9)	0.0819 (12)	0.0763 (11)	−0.0047 (8)	−0.0061 (7)	−0.0012 (9)
C11	0.0402 (9)	0.0687 (10)	0.0509 (8)	−0.0046 (7)	0.0035 (7)	−0.0054 (8)
C12	0.0613 (12)	0.0988 (16)	0.1354 (18)	0.0114 (10)	−0.0029 (12)	−0.0533 (14)

Geometric parameters (Å, °)

C9—O1	1.2220 (18)	C3—C4	1.391 (2)
C11—O2	1.2328 (17)	C4—C5	1.376 (2)
N1—C9	1.3444 (19)	C4—H4	0.9300
N1—C6	1.4026 (19)	C5—C6	1.389 (2)
N1—H1	0.8600	C5—H5	0.9300
N2—C11	1.404 (2)	C6—C7	1.389 (2)
N2—C9	1.412 (2)	C7—C8	1.385 (2)
N2—C10	1.4677 (18)	C7—H7	0.9300
N3—C11	1.326 (2)	C8—H8	0.9300
N3—C12	1.451 (2)	C10—H10A	0.9600
N3—H3	0.8600	C10—H10B	0.9600
C1—C2	1.173 (2)	C10—H10C	0.9600
C1—H1A	0.9300	C12—H12A	0.9600
C2—C3	1.443 (2)	C12—H12B	0.9600
C3—C8	1.381 (2)	C12—H12C	0.9600
C9—N1—C6	128.52 (13)	C8—C7—H7	120.2
C9—N1—H1	115.7	C6—C7—H7	120.2
C6—N1—H1	115.7	C3—C8—C7	121.61 (15)

C11—N2—C9	124.21 (12)	C3—C8—H8	119.2
C11—N2—C10	119.76 (14)	C7—C8—H8	119.2
C9—N2—C10	116.02 (12)	O1—C9—N1	124.52 (16)
C11—N3—C12	119.84 (15)	O1—C9—N2	119.63 (14)
C11—N3—H3	120.1	N1—C9—N2	115.85 (13)
C12—N3—H3	120.1	N2—C10—H10A	109.5
C2—C1—H1A	180.0	N2—C10—H10B	109.5
C1—C2—C3	178.2 (2)	H10A—C10—H10B	109.5
C8—C3—C4	118.44 (15)	N2—C10—H10C	109.5
C8—C3—C2	121.54 (15)	H10A—C10—H10C	109.5
C4—C3—C2	120.01 (15)	H10B—C10—H10C	109.5
C5—C4—C3	120.42 (15)	O2—C11—N3	120.71 (14)
C5—C4—H4	119.8	O2—C11—N2	122.42 (15)
C3—C4—H4	119.8	N3—C11—N2	116.87 (13)
C4—C5—C6	120.97 (14)	N3—C12—H12A	109.5
C4—C5—H5	119.5	N3—C12—H12B	109.5
C6—C5—H5	119.5	H12A—C12—H12B	109.5
C5—C6—C7	118.91 (15)	N3—C12—H12C	109.5
C5—C6—N1	116.33 (13)	H12A—C12—H12C	109.5
C7—C6—N1	124.74 (14)	H12B—C12—H12C	109.5
C8—C7—C6	119.64 (15)		
N1—C9—N2—C11	−5.7 (2)	O2—C11—N2—C10	−175.88 (14)
C9—N2—C11—N3	−176.34 (13)	O1—C9—N2—C11	174.09 (14)
N2—C11—N3—C12	−176.20 (16)	C9—N2—C11—O2	3.2 (2)
N1—C9—N2—C10	173.37 (12)	O2—C11—N3—C12	4.3 (3)
O1—C9—N2—C10	−6.8 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.86	1.82	2.5451 (17)	141
N3—H3···O1^{i}	0.86	2.20	2.9245 (17)	141

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+1/2.

Fig. 1