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4-(Phenylhydrazonomethyl)benzonitrile

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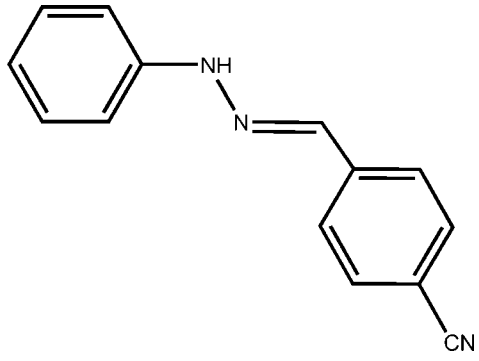
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.058; wR factor = 0.170; data-to-parameter ratio = 10.2.

The title compound, $C_{14}H_{11}N_3$, was synthesized by the reaction of phenylhydrazine and 4-formylbenzonitrile. The molecule adopts an E configuration with respect to the N=N bond. The dihedral angle between the two benzene rings is 13.56 (15)°. In the crystal structure, intermolecular N—H···N hydrogen bonds form one-dimensional chains along the b axis.

Related literature

For the preparation of tetrazole derivatives from nitrile compounds, see: Drew *et al.* (1984); Dunica *et al.* (1991); Szczesna & Urbanczyk-Lipkowska (2002); Wittenberger & Donner (1993). For the general chemistry of tetrazole compounds, see: Xiong *et al.* (2002).



Experimental

Crystal data

$C_{14}H_{11}N_3$
M_r = 221.26
Orthorhombic, $P2_12_12_1$
a = 7.1442 (14) Å
b = 11.147 (2) Å
c = 14.726 (3) Å
V = 1172.7 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 (2) K
0.2 × 0.08 × 0.08 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.812, T_{max} = 1.000
(expected range = 0.807–0.994)
11983 measured reflections
1565 independent reflections
984 reflections with $I > 2\sigma(I)$
R_{int} = 0.074

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.170
S = 1.09
1565 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2B···N3^{i}	0.90	2.56	3.313 (5)	141

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2419).

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supplementary materials

Acta Cryst. (2007). E**63**, o4750 [**doi:10.1107/S1600536807057984**]

4-(Phenylhydrazonomethyl)benzonitrile

G.-X. Wang and H.-Y. Ye

Comment

Nitrile compounds are the precursor of tetrazole derivatives (Dunica, *et al.*, 1991; Wittenberger, *et al.*, 1993), which we have focused on for the design of noncentrosymmetric bulk materials (Xiong, *et al.*(2002)). We report here the crystal structure of the title compound, 4-(phenyl-hydrazonomethyl)benzonitrile, (I), Fig. 1.

In I, the C=N double bond (1.359 (4) Å) is in the range 1.34–1.38 Å found in other similar hydrazone complexes with a *trans* configuration (Szczesna & Urbanczyk-Lipkowska (2002); Drew,*et al.*(1984). The torsion angles of C9 - N2 - N1 - C1 is −178.7 (3)°. Dihedral angle between the two benzene rings is 13.56 (0.15) °. In the crystal structure molecules related by translation along *b* axis are connected by N2—H2B···N3 hydrogen bonds resulting in the formation of one dimensional chains along the *b* axis.

Experimental

To a solution of 4-formylbenzonitrile (6.55 g, 0.05 mol) in methanol (40 ml) was added phenylhydrazine (5.40 g, 0.05 mol) with stirring at room temperature. After 20 minutes, a mass of yellow precipitate appeared and was filtered. The crude product was recrystallized by slowly evaporating an ethanol solution to yield pale yellow block-like crystals, suitable for X-ray analysis.

Refinement

Positional parameters of all the H atoms were calculated geometrically and were allowed to ride on the C atoms to which they are bonded, with d(C—H) = 0.93 and d(N—H) = 0.90Å and U_{iso}(H) = 1.2Ueq(C or N). In the absence of significant anomalous scattering effects, Friedel pairs were merged.

Figures

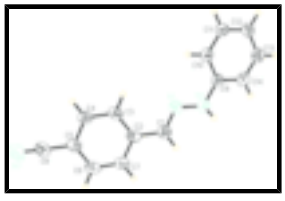

Fig. 1. A view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

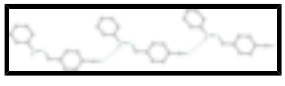

Fig. 2. A view of the chain structure of the molecules related by translation along *b* axis and all hydrogen atoms not involved in hydrogen bonding (dashed lines) were omitted for clarity.

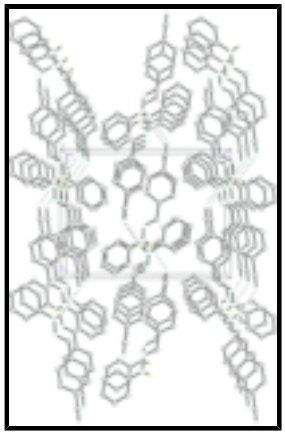

Fig. 3. The crystal packing of the title compound viewed along the *a* axis. all hydrogen atoms not involved in hydrogen bonding (dashed lines) were omitted for clarity.

4-(Phenylhydrazonomethyl)benzonitrile

Crystal data

$C_{14}H_{11}N_3$	F_{000} = 464
M_r = 221.26	D_x = 1.253 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 9243 reflections
a = 7.1442 (14) Å	θ = 3.2–27.5º
b = 11.147 (2) Å	μ = 0.08 mm^{-1}
c = 14.726 (3) Å	T = 293 (2) K
V = 1172.7 (4) Å^3	Block, yellow
Z = 4	0.2 × 0.08 × 0.08 mm

Data collection

Mercury2 diffractometer	1565 independent reflections
Radiation source: fine-focus sealed tube	984 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.074
T = 293(2) K	θ_{max} = 27.5º
ω scans	θ_{min} = 3.2º
Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)	h = −9→9
T_{min} = 0.812, T_{max} = 1.0	k = −14→14
11983 measured reflections	l = −19→19

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0863P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.058	$(\Delta/\sigma)_{max}$ = <0.001

$wR(F^2) = 0.170$

$S = 1.09$

1565 reflections

154 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$\Delta\rho_{max} = 0.14$ e Å^{-3}

$\Delta\rho_{min} = -0.14$ e Å^{-3}

Extinction correction: none

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}
N1	0.4559 (4)	0.4066 (3)	0.51082 (19)	0.0665 (8)
N2	0.4212 (5)	0.2870 (3)	0.5177 (2)	0.0756 (9)
H2B	0.4864	0.2514	0.4729	0.091*
N3	0.4871 (6)	1.0614 (3)	0.3748 (2)	0.1010 (13)
C1	0.4160 (5)	0.4567 (3)	0.4354 (2)	0.0671 (9)
H1	0.3704	0.4100	0.3880	0.081*
C2	0.4400 (4)	0.5844 (3)	0.4218 (2)	0.0606 (9)
C3	0.5107 (5)	0.6589 (3)	0.4901 (2)	0.0639 (9)
H3	0.5493	0.6256	0.5449	0.077*
C4	0.5241 (5)	0.7814 (3)	0.4772 (2)	0.0674 (10)
H4	0.5704	0.8301	0.5233	0.081*
C5	0.4680 (5)	0.8315 (3)	0.3950 (2)	0.0642 (9)
C6	0.4008 (5)	0.7585 (3)	0.3266 (2)	0.0704 (10)
H6	0.3649	0.7915	0.2713	0.084*
C7	0.3871 (5)	0.6374 (4)	0.3406 (2)	0.0675 (10)
H7	0.3410	0.5892	0.2941	0.081*
C8	0.4797 (6)	0.9587 (4)	0.3826 (2)	0.0759 (11)
C9	0.4638 (5)	0.2253 (3)	0.5963 (2)	0.0606 (8)
C10	0.5663 (5)	0.2755 (3)	0.6664 (2)	0.0657 (9)
H10	0.6101	0.3538	0.6618	0.079*
C11	0.6031 (5)	0.2089 (3)	0.7430 (2)	0.0732 (10)
H11	0.6708	0.2436	0.7902	0.088*
C12	0.5428 (6)	0.0933 (3)	0.7515 (3)	0.0745 (11)

H12	0.5711	0.0490	0.8032	0.089*
C13	0.4383 (6)	0.0427 (3)	0.6814 (3)	0.0752 (11)
H13	0.3935	−0.0353	0.6866	0.090*
C14	0.4019 (5)	0.1080 (3)	0.6053 (2)	0.0703 (10)
H14	0.3340	0.0732	0.5583	0.084*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0649 (17)	0.0672 (19)	0.0674 (19)	0.0050 (15)	−0.0015 (15)	0.0044 (14)
N2	0.090 (2)	0.069 (2)	0.0686 (19)	0.0038 (19)	−0.0102 (17)	−0.0012 (15)
N3	0.131 (3)	0.089 (2)	0.083 (2)	0.003 (3)	0.007 (2)	0.0146 (19)
C1	0.067 (2)	0.075 (2)	0.060 (2)	−0.0034 (19)	−0.0108 (18)	−0.0002 (18)
C2	0.0475 (17)	0.084 (2)	0.0508 (19)	0.0019 (18)	−0.0020 (15)	0.0015 (16)
C3	0.0601 (19)	0.077 (3)	0.054 (2)	−0.0017 (18)	−0.0092 (17)	0.0133 (17)
C4	0.061 (2)	0.082 (3)	0.059 (2)	−0.007 (2)	−0.0104 (17)	0.0004 (17)
C5	0.057 (2)	0.077 (2)	0.058 (2)	0.0018 (19)	0.0046 (17)	0.0081 (17)
C6	0.068 (2)	0.096 (3)	0.0477 (19)	0.007 (2)	−0.0026 (18)	0.0090 (19)
C7	0.068 (2)	0.088 (3)	0.0472 (18)	−0.003 (2)	−0.0016 (18)	0.0006 (17)
C8	0.078 (3)	0.079 (3)	0.070 (2)	0.005 (2)	0.009 (2)	0.013 (2)
C9	0.0610 (18)	0.059 (2)	0.062 (2)	0.0036 (17)	−0.0030 (16)	−0.0030 (15)
C10	0.073 (2)	0.0580 (19)	0.066 (2)	0.0036 (19)	−0.005 (2)	−0.0059 (17)
C11	0.088 (3)	0.072 (2)	0.060 (2)	0.019 (2)	−0.0115 (19)	−0.0099 (18)
C12	0.090 (3)	0.065 (2)	0.068 (2)	0.017 (2)	0.007 (2)	0.0052 (17)
C13	0.090 (3)	0.061 (2)	0.075 (2)	−0.004 (2)	0.009 (2)	0.0017 (18)
C14	0.072 (2)	0.069 (2)	0.070 (2)	−0.002 (2)	0.0021 (19)	−0.0084 (18)

Geometric parameters (Å, °)

N1—C1	1.275 (4)	C6—C7	1.370 (4)
N1—N2	1.359 (4)	C6—H6	0.9300
N2—C9	1.381 (4)	C7—H7	0.9300
N2—H2B	0.9000	C9—C10	1.384 (4)
N3—C8	1.151 (4)	C9—C14	1.387 (4)
C1—C2	1.448 (4)	C10—C11	1.375 (4)
C1—H1	0.9300	C10—H10	0.9300
C2—C7	1.387 (4)	C11—C12	1.365 (5)
C2—C3	1.399 (4)	C11—H11	0.9300
C3—C4	1.382 (4)	C12—C13	1.393 (5)
C3—H3	0.9300	C12—H12	0.9300
C4—C5	1.393 (5)	C13—C14	1.361 (5)
C4—H4	0.9300	C13—H13	0.9300
C5—C6	1.381 (4)	C14—H14	0.9300
C5—C8	1.433 (5)		
C1—N1—N2	117.0 (3)	C6—C7—C2	122.0 (3)
N1—N2—C9	120.7 (3)	C6—C7—H7	119.0
N1—N2—H2B	106.5	C2—C7—H7	119.0
C9—N2—H2B	106.3	N3—C8—C5	178.3 (4)

N1—C1—C2	121.7 (3)	N2—C9—C10	122.8 (3)
N1—C1—H1	119.2	N2—C9—C14	118.6 (3)
C2—C1—H1	119.2	C10—C9—C14	118.6 (3)
C7—C2—C3	117.8 (3)	C11—C10—C9	119.7 (3)
C7—C2—C1	120.4 (3)	C11—C10—H10	120.2
C3—C2—C1	121.8 (3)	C9—C10—H10	120.2
C4—C3—C2	120.8 (3)	C12—C11—C10	121.6 (3)
C4—C3—H3	119.6	C12—C11—H11	119.2
C2—C3—H3	119.6	C10—C11—H11	119.2
C3—C4—C5	119.7 (3)	C11—C12—C13	118.9 (3)
C3—C4—H4	120.1	C11—C12—H12	120.5
C5—C4—H4	120.1	C13—C12—H12	120.5
C6—C5—C4	119.9 (3)	C14—C13—C12	119.8 (4)
C6—C5—C8	120.7 (3)	C14—C13—H13	120.1
C4—C5—C8	119.4 (3)	C12—C13—H13	120.1
C7—C6—C5	119.7 (3)	C13—C14—C9	121.4 (4)
C7—C6—H6	120.1	C13—C14—H14	119.3
C5—C6—H6	120.1	C9—C14—H14	119.3
C9—N2—N1—C1	178.7 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2B···N3^{i}	0.90	2.56	3.313 (5)	141

Symmetry codes: (i) *x*, *y*−1, *z*.

Fig. 1

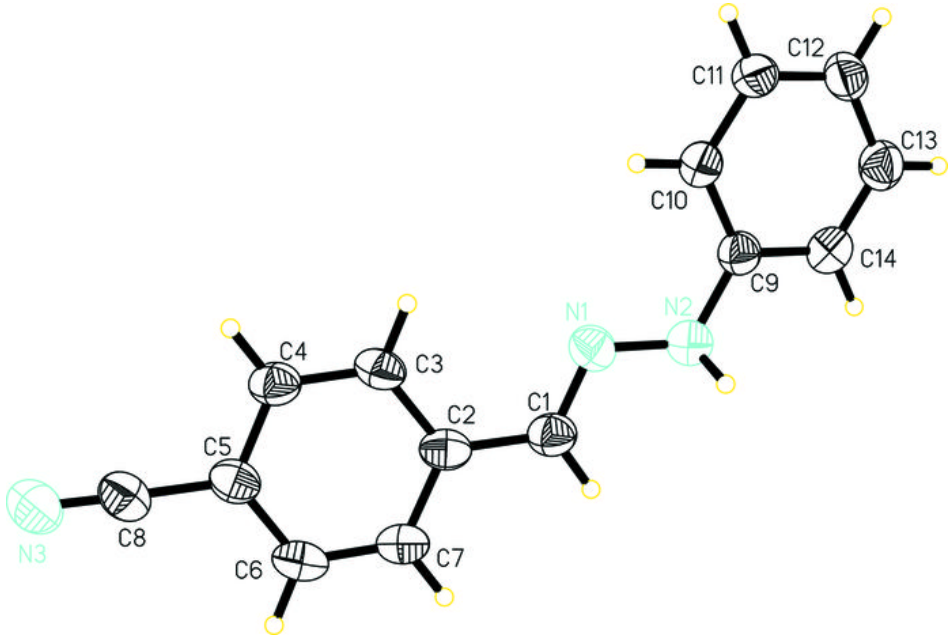

Fig. 2

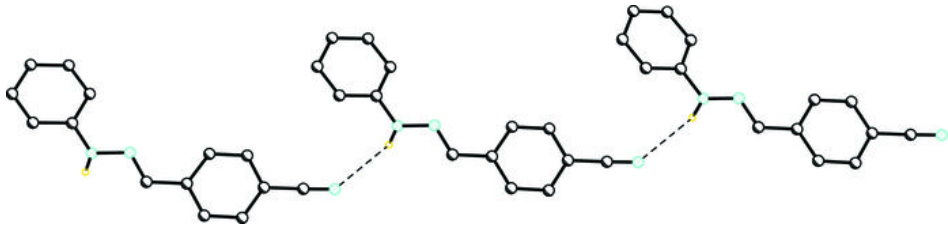

Fig. 3