

***N*-(4-Nitrobenzylidene)-*N'*-phenylhydrazine**Tuncay Tunc,^a Habibe Tezcan,^b Musa Sarı,^{a*} Orhan Büyükgüngör^c and Rahmi Yağbasan^a^aDepartment of Physics Education, Gazi University, Beşevler, 06500 Ankara, Turkey,^bDepartment of Chemistry Education, Gazi University, Beşevler, 06500 Ankara, Turkey, and ^cDepartment of Physics, Ondokuzmayıs University, TR-55139, Samsun, Turkey

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Received 9 June 2003

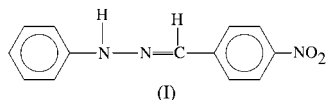
Accepted 21 July 2003

Online 16 August 2003

Molecules of the title compound (alternative name: *p*-nitrobenzaldehyde phenylhydrazone), C₁₃H₁₁N₃O₂, adopt an *E* configuration about the azomethine C=N double bond. Molecules are approximately planar and the dihedral angle between the planes of the phenyl rings is 11.62 (9)°. Hydrogen bonding links molecules related by 4₂ screw axes to form helices with a pitch of 7.7186 (8) Å.

Comment

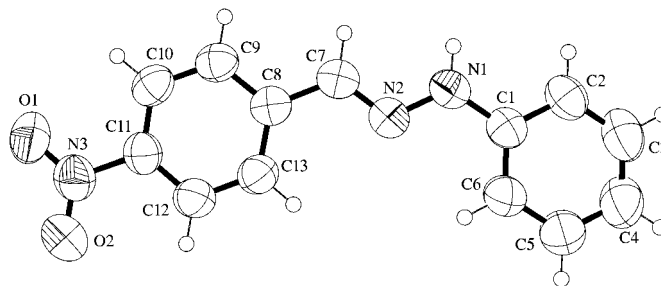
Hydrazones are formed when hydrazines condense with aldehydes and ketones, *e.g.* by the condensation of aldehydes (or substituted aldehydes) with phenylhydrazine at a pH of 4–5 (McMurry, 1999), and typically are crystalline compounds with sharp melting points. Hydrazones are frequently more efficient than oximes in this reaction since their greater molecular weight causes a lower solubility in most solvents and they can, therefore, often be more easily isolated and recrystallized. Hydrazones have been widely studied as chelating ligands for the spectrophotometric and fluorimetric determination of trace metal ions (Katyal & Dutt, 1975; Galiano-Roth & Collum, 1988). Many of these compounds have found widespread application in medicine, technology and analytical chemistry (Kitaev, 1977).



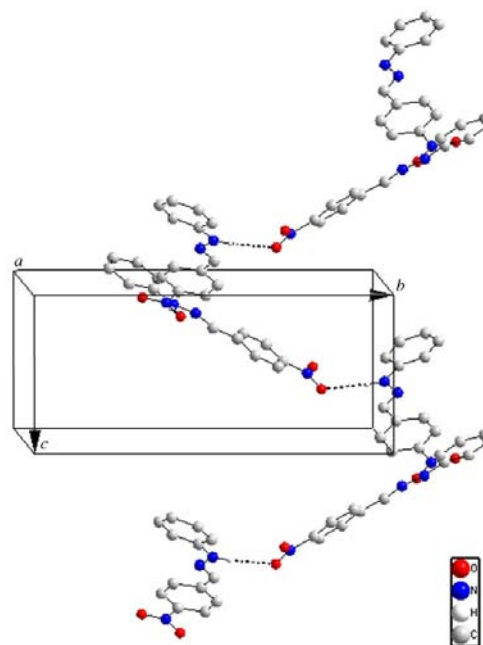
Molecules of the title compound, (I), adopt an *E* configuration about the azomethine C=N double bond, with an N1–N2–C7–C8 torsion angle of 178.67 (11)°. The N1–N2 [1.3479 (14) Å], O1–N3 [1.2188 (15) Å] and O2–N3 [1.2185 (14) Å] bond lengths, which are consistent with those of 1.216 (8) and 1.214 (7) Å in 2-nitrobenzaldehyde methylhydrazone, indicate that these bonds correspond to double

and single bonds. The dihedral angle between the planes of the phenyl rings is 11.62 (9)°, and the nitrophenyl and phenyl rings make dihedral angles with the central hydrazone bridge (N1/N2/C7) of 3.25 (11) and 9.47 (13)°, respectively. There is only slight asymmetry in the exocyclic angles at C11 [C12–C11–N3 = 119.68 (13)° and C10–C11–N3 = 118.40 (13)°], in contrast to the situation in 2-nitrobenzaldehyde phenylhydrazone (Tosi *et al.*, 1988), where enhanced asymmetry is ascribed to steric contacts involving the 2-nitro group. The more pronounced asymmetry at C8 [C13–C8–C7 = 122.35 (12)° and C9–C8–C7 = 119.55 (12)°] is also seen in studies with a methoxy group on the phenyl ring (Shanmuga Sundara Raj *et al.*, 1999, 2000; Tunc *et al.*, 2003).

Intermolecular hydrogen bonding between the H atom on atom N1 of the hydrazone bridge and atom O1 of a nitro group related by the 4₂ screw axis links molecules into helices with a pitch of 7.7186 (8) Å running along the *c* axis (Fig. 2).

**Figure 1**

The molecular structure and atomic labelling scheme of the title compound (ORTEP-3; Farrugia, 1997). Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

A packing diagram showing the hydrogen bonding (dotted lines) which links molecules related by 4₂ screw axes into helices.

The N—H···O and N···O distances are short compared with the sum of the relevant van der Waals radii (Bondi, 1964).

Experimental

A solution of 4-nitrobenzaldehyde (3.02 g, 0.02 mol) in hot methanol (50 ml) was added dropwise to a solution of phenylhydrazine (2.16 g, 0.02 mol) in hot methanol (50 ml) at a pH of 5–6. The resulting red solid was filtered off, dried and recrystallized after refluxing in hot methanol for 3 h. The red crystals thus obtained were filtered off and dried in air.

Crystal data

C ₁₃ H ₁₁ N ₃ O ₂	Mo K α radiation
$M_r = 241.25$	Cell parameters from 2629 reflections
Tetragonal, $P4_2/n$	$\theta = 1.7\text{--}27.2^\circ$
$a = 17.5017 (17) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 7.7186 (8) \text{ \AA}$	$T = 293 (2) \text{ K}$
$V = 2364.3 (4) \text{ \AA}^3$	Square prism, dark red
$Z = 8$	$0.40 \times 0.40 \times 0.25 \text{ mm}$
$D_x = 1.355 \text{ Mg m}^{-3}$	

Data collection

Stoe IPDS-2 diffractometer	$R_{\text{int}} = 0.038$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.2^\circ$
Absorption correction: by integration (<i>X-RED</i> ; Stoe & Cie, 2002)	$h = -22 \rightarrow 22$
$T_{\text{min}} = 0.963$, $T_{\text{max}} = 0.977$	$k = -22 \rightarrow 22$
2636 measured reflections	$l = -9 \rightarrow 9$
2629 independent reflections	1 standard reflection
1280 reflections with $I > 2\sigma(I)$	frequency: 30 min
	intensity decay: 5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.070$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.09 \text{ e \AA}^{-3}$
2629 reflections	$\Delta\rho_{\text{min}} = -0.11 \text{ e \AA}^{-3}$
164 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.010 (2)

Table 1

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

O1—N3	1.2188 (15)	N2—C7	1.2826 (15)
O2—N3	1.2185 (14)	N3—C11	1.4637 (17)
N1—N2	1.3479 (14)	C7—C8	1.4494 (17)
N1—C1	1.3823 (16)		
N2—N1—C1	120.58 (11)	N2—C7—C8	121.21 (12)
C7—N2—N1	117.67 (11)	C9—C8—C7	119.55 (12)
O2—N3—O1	122.38 (14)	C13—C8—C7	122.35 (12)
O2—N3—C11	118.64 (14)	C12—C11—N3	119.68 (13)
O1—N3—C11	118.98 (13)	C10—C11—N3	118.40 (13)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N1—H1···O1 ⁱ	0.86	2.29	3.115 (2)	162

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

H atoms were placed geometrically at distances of 0.86 and 0.93 \AA from their parent atoms for N—H and Csp^2 —H bonds, respectively. In the refinement, a riding model was used for all H atoms, with $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXS97*.

The authors wish to acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS-2 diffractometer purchased under grant F.279 of the University Research Fund.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1538). Services for accessing these data are described at the back of the journal.

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