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Nota técnica

(*E*)-2-(4-methoxybenzylidene)-1-(2-nitrophenyl)hydrazine

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Resumen

El compuesto (*E*)-2-(4-metoxibencilideno)-1-(2-nitrofenil) hidracina (I), $C_{14}H_{13}N_3O_3$, ha sido sintetizado y caracterizado por espectroscopia IR y RMN y difracción de rayos-X. El compuesto cristaliza en el sistema monoclínico, grupo espacial $P2_1/c$, con parámetros de celda ***a***=12,7671 (18) Å, ***b***= 5,3718 (7) Å, ***c*** = 19,887 (3) Å, β=104,138 (4), V=1322,6 (3) Å^3. El compuesto I, muestra dos (2) enlaces de hidrógeno intermoleculares los cuales son descritos por el grafo $R^2_2(12)$ y $R^1_2(6)$. En el empaquetamiento cristalino las moléculas se producen y apilan alternadamente a lo largo el eje ***b*** a través de una interacción N3—O2⋯*Cg* (1).

Palabras clave: hidracina, estructura cristalina.

Abstract

The title compound, (*E*)-2-(4-methoxybenzylidene)-1-(2-nitrophenyl)hydrazine (I), $C_{14}H_{13}N_3O_3$, has been synthesized and characterized by IR and NMR spectroscopy, and X-ray diffraction. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with unit-cell parameters ***a***=12.7671 (18) Å, ***b***= 5.3718 (7) Å, ***c***= 19.887 (3) Å, β=104.138 (4), V=1322.6 (3) Å^3. Compound 1 shows two intermolecular hydrogen bonds patterns which are described by the graph set symbol $R^2_2(12)$ and $R^1_2(6)$. The molecules are stacked alternately along the ***b*** -axis through N3—O2⋯*Cg* (1) interactions.

Keywords: Hydrazine, crystal structure

Introducción

N-Benzylidene-hydrazines (hydrazones) have been studied for many years due to their ease of synthesis, their increased stability with respect to imines and their tendency to form good crystals[1-3]. Hydrazones are key building blocks for the synthesis of heterocyclic compounds having biological and pharmaceutical activities[4-7], and their application as switches and the colorimetric cell construction solares[8].

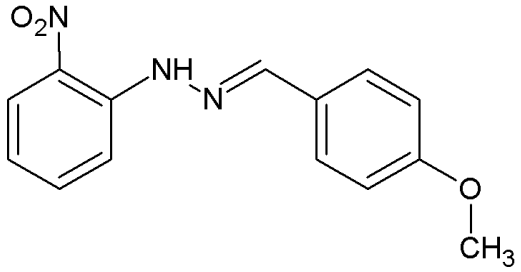

Fig. 1. Molecular diagram of (*E*)-2-(4-methoxybenzylidene)-1-(2-nitrophenyl)hydrazine (**I**)

Materials and methods

General Experimental Procedures.

Melting points were determined on a digital IA-9100 ELECTROTHERMAL fusiometer. The IR spectrum was recorded on a Perkin Elmer FT-IR instrument model FTIR-Prestige21 in a KBr pellet. ^{1}H NMR ^{13}CNMR spectra were measured with a Bruker biospin 500 MHz spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (Me_4Si, d = 0) in DMSO-d_6; *J* values are given in Hz. The following abbreviations are used: s, singlet; d, doublet; q, quartet; dd, doublet of doublet; t, triplet; m, multiplet; br s, broad signal.

The structure was solved and refined using the Bruker *SHELXTL*[9] Software Package, cell refinement and data reduction with Bruker *SAINT* [10] using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{14}H_{14}N_3O_3$. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed in calculated positions and refined using a *riding model* with their thermal

parameters equal to C—H = 0.93 Å, Uiso(H) =1.2 Ueq(C) for aryl H and C—H = 0.96 Å Uiso(H) =1.5 Ueq(C) for methyl H.

The final anisotropic full-matrix least-squares refinement on F2 with 182 variables converged at R1 = 5.37%, for the observed data and wR2 = 15.00% for all data. The goodness-of-fit was 0.911. The largest peak in the final difference electron density synthesis was 0.176 e-/Å3 and the largest hole was -0.226 e-/Å3 with an RMS deviation of 0.046 e-/Å3. On the basis of the final model, the calculated density was 1.362 g/cm3 and F(000), 568 e-.

Synthesis of (E)-2-(4-methoxybenzylidene)-1-(2-nitrophenyl)hydrazine (I).

A mixture of 4-nitrophenylhydrazine hydrochloride (3 mmol) and 4-methoxybemzaldehyde (3 mmol) in water (10 ml) was irradiated using microwave radiation at 1250 W, with a heating rate of 25 to 80 °C for one minute, followed by heating for 3 minutes at 80 °C. The reaction mixture was cooled and filtered, washed with cold water and finally dried.

Results and discussion

The title compound (*E*)-2-(4-methoxybenzylidene)-1-(2-nitrophenyl)hydrazine (Fig. 1) was recrystallized from ethanol/ace-tone (8:2). yield (98%); Atom economy (79%); mp (487–488 K). FTIR (KBr, disk) ν, cm^{-1}: 3204 (N-H), 1613 (N=C), 1440-1306 (NO_2); mp: 232-233 °C; ^{1}H RMN (DMSO-d6, 500 MHz) δ: 11.09 (s, 1H, NH), 8.42 (s, 1H, N=CH), 8.09 (dd, 1H, J= 1.3 Hz, J= 7.8 Hz), 7.95 (dd, 1H, J= 1.3 Hz, J= 7.8 Hz), 7.69 (d, 2H, J= 8.8 Hz), 7.63 (m, 1H), 7.01 (d, 2H, J= 8.8 Hz), 6.87 (m, 1H), 3.22 (s, 3H, OCH_3); ^{13}C RMN (DMSO-d_6, 125 MHz) δ: 160.5, 145.2, 141.5, 136.4, 130.4, 128.4, 127.1, 125.7, 117.9, 115.9, 114.4, 55.3 (OCH_3); HRMS (*EI*) m/z cald for $C_{14}H_{13}N_3O_3$ (M+): 271,0957. Found: 271, 0953.

X-ray Crystal Structure Analysis of I.

The details of crystal data and refinement are given in Table 1. Fig. 2 shows the atom arrangements and the atom numbering scheme. All figures were drawn using the Diamond software[11].

A search of the Cambridge Structural Database (CSD)[12] revealed a compound N-(2,4-Dinitrophenyl)-N'-(4-methoxybenzylidene)hydrazine (Refcode YEFFAR) isomeric and isomorphous with 1: the difference between compounds YEFFAR and **I** is the location of the nitro substituent in the benzene ring.

Fig. 2 shows the molecular structure of compound (I) with the atom and ring numbering scheme. The molecular structure is completely planar. The ring–A is formed by atoms C1-C2-C3-C4-C5-C6 and ring-B is formed by atoms-C2a-C1a-C3a-C4a-C5a-C6a.

Table 1. Crystal data and refinement for Compound (**I**)

Crystal Data	
Formula	C14H13N3O3
Formula Weight	271.27
Crystal System	Monoclinic
Space group	P21/c (No. 14)
a, b, c (Å)	12.7671(18)
	5.3718(7)
	19.887(3)
α, β, γ (°)	90
	104.138(4)
	90
V(Å^3)	1322.6(3)
Z	4
D_{calc} (g/cm^3)	1.362
Mu(CuKα)	0.098
F(000)	568
Crystal Size(mm)	0.02 x 0.05 x 0.05
Data Collection	
Temperature (K)	296
Radiation (Å)	MoKa 0.71073
Theta Min-Max [Deg]	1.6, 27.5
Dataset	-16: 16 ; -6: 6 ; -25: 25
Tot., Uniq. Data, R(int)	11415, 3009, 0.081
Observed data [I >0.0sigma(I)]	1070
Refinement	
Nref, Npar	3009, 182
R, wR2, S	0.054, 0.150, 0.91
Min. and Max. Resd. Dens.[e/Å^3]	-0.23, 0.18

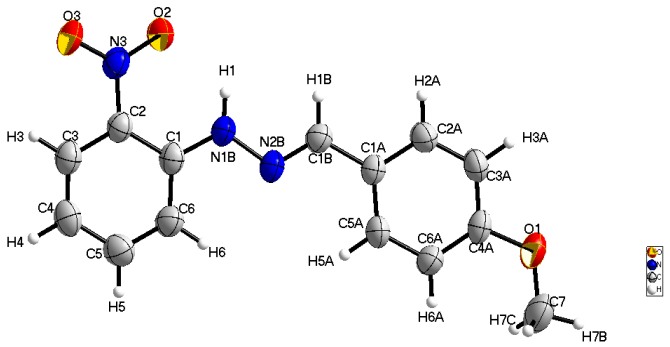

Fig. 2. Molecular structure of (*E*)-2-(4-methoxybenzylidene)-1-(2-nitrophenyl)hydrazine (**I**)

The bond distances (Table 2) within A-ring and B-ring are consistent with aromatic delocalization.

There are two intramolecular hydrogen bonds: N1b—H1b ⋯ O2 [1.99 Å, 127 °], and C6—H6 ⋯ N2B [2.39 Å, 101 °], which create rings with graph set symbols of S(6) and S(5), respectively[13]. Table 3 shows the geometrical parameters of the two intermolecular hydrogen bonds observed in the crystal structure.

Table 2. Selected bond distances (Å) and angles (º) for compound **I.**

C1-C6	1.402(6)	C1a-C2a	1.389(5)
C1-C2	1.411(5)	C2a-C3a	1.367(6)
C2-C3	1.396(5)	C3a-C4a	1.376(6)
C3-C4	1.357(6)	C4a-C6a	1.379(6)
C4-C5	1.387(6)	C5a-C6a	1.377(5)
C5-C6	1.369(6)	C1a-C5a	1.376(6)
N1b-N2b	1.381(5)	N2b-C1b	1.275(5)
N2b-N1b-C1	118.2(3)	N1b-N2b-C1b	115.7(3)
N2b-C1b-C1A	122.0(4)	O2-N3-C2	119.2(3)
O3-N3-C2	119.6(3)	C4a-O1-C7	118.2(3)

In the crystal packing (Fig. 3), two intermolecular hydrogen bonds are present: N1b—H1···O2 [2.56 Å, 156 °] and C1B—H1b···O2 [2.55 Å, 157°]. In these hydrogen bonds, atom O2 acts as a bifurcated acceptor. Pairs of the N1B—H1 ··· O2 hydrogen bonds [2.56 Å, 156 °] generate centrosymmetric dimers, with $R^2_2(12)$ rings[13]. Meanwhile pairs of the C1b—H1b···O2 hydrogen bond [2.55 Å, 157 °], generates $R^1_2(6)$ rings.

As shown in fig. 4, the molecules are stacked along the ***b*** -axis through N3—O2···*Cg* (1) interactions [3.409(3) Å, 96.41(15) °] (*Cg(1)* is the centroid of the ring-A at *x,-1 + y, z)* between the oxygen atom of the nitro group of one molecule, and the π-system of the nitrobenzyl moiety of another molecule.

This type of interaction was also observed in the isostructural compound N-(2,4-Dinitrophenyl)-N'-(4-methoxybenzylidene)hydrazine with Refcode Yeffar[14].

Table 3. Hydrogen bonds and short contacts for compound I. Cg1 is the centroid of the ring-A

Bond	**D-H**	**H-A**	**D-A**	**D-H-A**	**Symmetry**	**Graph set**
N1b--H1...O2	0.86	2.00	2.606(4)	127		S(6)
N1b--H1...O2	0.86	2.56	3.366(4)	156	1-x, 1-y, 2-z	$R^2_2(12)$
C1b--H1b...O2	0.93	2.54	3.422(5)	158	1-x, 1-y, 2-z	$R^1_2(6)$
C6--H6...N2b	0.93	2.38	2.712(5)	101		S(5)
Short Contacts Y-X...Cg	**Y-X**	**X…Cg**	**Y…Cg**	**Y-X-Cg**	**Symmetry**	
N3—O2···*Cg* (1)	1.237(4)	3.410(3)	3.757(4)	96.5(2)	x, 1+y, z	

For this compound, which exhibits geometric parameters [3.2709 (18) Å, 91.86 (7) º], the interaction occurs between the oxygen of the nitro group of one molecule and the methoxybenzene ring of another molecule.

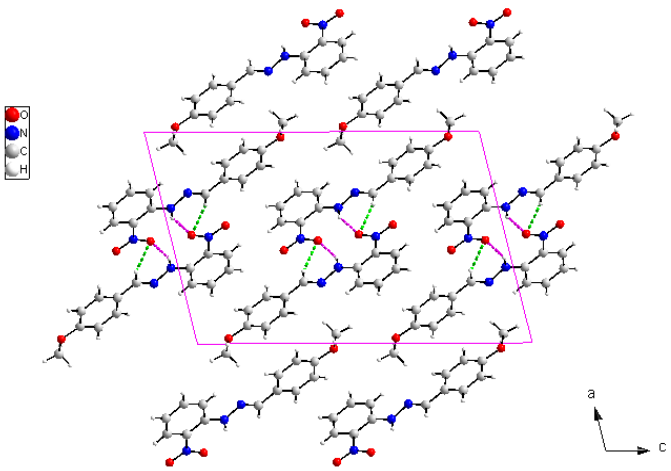

Fig. 3. Hydrogen bonding patterns present in (*E*)-2-(4-methoxybenzylidene)-1-(2-nitrophenyl)hydrazine (I) along b-axis

The CSD lists 39 reports of N3—O2···π interactions. While in the compound with Refcode Yeffar[14], there are π-π interactions between the two aryl groups, such an interaction is absent in compound 1.

The packing index is 68.6% and not solvent accessible void in the structure

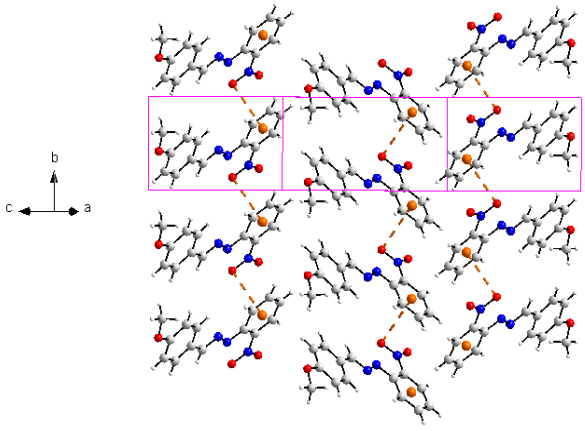

Fig. 4. Short Contacts Y-X...Cg presents in compound (I) in the direction [1, 0, 1]

Conclusions

The structural analysis of (*E*)-2-(4-methoxybenzylidene)-1-(2-nitrophenyl)hydrazine (I), was established by single crystal X-ray diffraction, and this is the first X-ray report of this compound.

Supporting Information Available

CCDC 953347contains the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ products/csd/request/ (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam. ac.uk).

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