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(E)-2-(4-methoxybenzylidene)-1-(2-nitrophenyl)hydrazine
Avances en Química, vol. 8, núm. 3, septiembre-diciembre, 2013, pp. 167-170
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Available in: http://www.redalyc.org/articulo.oa?id=93330145003
**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. Hydrazones are key building blocks for the synthesis of heterocyclic compounds having biological and pharmaceutical activities, and their application as switches and the colorimetric cell construction solares.

![Fig. 1. Molecular diagram of (E)-2-(4-methoxybenzylidene)-1-(2-nitrophenyl)hydrazine (I)](image)

**Materiales y métodos**

General Experimental Procedures.

Melting points were determined on a digital IA-9100 ELECTROTHERMAL fusimeter. The IR spectrum was recorded on a Perkin Elmer FT-IR instrument model FTIR-Prestige21 in a KBr pellet. ^H NMR and ^1^C NMR spectra were measured with a Bruker biospin 500 MHz spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (Me₄Si, d = 0) in DMSO-d₆; 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 Software Package, cell refinement and data reduction with Bruker SAINT using the space group P2₁/c, with Z = 4 for the formula unit, C₁₄H₁₃N₃O₅. 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 \((E)-2-(4\text{-methoxybenzylidene})-1-(2\text{-nitrophenyl})\text{hydrazine (I).}\)

A mixture of 4-nitrophenylhydrazine hydrochloride (3 mmol) and 4-methoxybenzaldehyde (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 \((E)-2-(4\text{-methoxybenzylidene})-1-(2\text{-nitrophenyl})\text{hydrazine (Fig. 1)}\) was recrystallized from ethanol/acetic acid (8:2), yield (98%); mp (487–488 °C); FTIR (KBr, disk) ν, cm⁻¹: 3204 (N-H), 1613 (C=O), 1585 (N-C), 1452, 1415, 1346, 1284, 1271, 1257, 1179, 1159, 1144, 1053, 1032, 986, 907, 874, 844, 768, 706, 679, 626, 531, 493, 472; ¹H RMN (DMSO-d₆, 600 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, OCH₃); ¹³C RMN (DMSO-d₆, 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 (OCH₃); HRMS (EI) m/z cald for C₁₄H₁₃N₃O₃ (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.

A search of the Cambridge Structural Database (CSD) revealed a compound N-(2,4-Dinitrophenyl)-N’-(4-methoxybenzylidene)hydrazine (Refcode YEFFAR) isomeric and isomorphous with I: 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)

<table>
<thead>
<tr>
<th>Crystal Data</th>
<th>Formula</th>
<th>C14H13N3O3</th>
<th>Formula Weight</th>
<th>271.27</th>
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<tbody>
<tr>
<td>Space group</td>
<td>P21/c</td>
<td>(No. 14)</td>
<td>a, b, c (Å)</td>
<td>12.7671(18)</td>
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<tr>
<td>a, b, c (Å)</td>
<td></td>
<td>5.3718(7)</td>
<td>19.887(3)</td>
<td></td>
</tr>
<tr>
<td>α, β, γ (°)</td>
<td></td>
<td>90</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>V(Å³)</td>
<td></td>
<td>104.138(4)</td>
<td>104.138(4)</td>
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<tr>
<td>Z</td>
<td></td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Dcalc (g/cm³)</td>
<td></td>
<td>1.362</td>
<td>1.362</td>
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<tr>
<td>Mu(CuKα)</td>
<td></td>
<td>0.098</td>
<td>0.098</td>
<td></td>
</tr>
<tr>
<td>F(000)</td>
<td></td>
<td>568</td>
<td>568</td>
<td></td>
</tr>
<tr>
<td>Crystal Size(mm)</td>
<td></td>
<td>0.02 x 0.05 x 0.05</td>
<td>0.02 x 0.05 x 0.05</td>
<td></td>
</tr>
</tbody>
</table>

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. Resid. Dens.[e/Å³] | -0.23, 0.18 |

Fig. 2. Molecular structure of \((E)-2-(4\text{-methoxybenzylidene})-1-(2\text{-nitrophenyl})\text{hydrazine (I).}\)

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. 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 (°) for compound I.

<table>
<thead>
<tr>
<th>Bond</th>
<th>D-H</th>
<th>H-A</th>
<th>D-A</th>
<th>D-H-A</th>
<th>Symmetry</th>
<th>Graph set</th>
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</thead>
<tbody>
<tr>
<td>N1b—H1...O2</td>
<td>0.86</td>
<td>2.00</td>
<td>2.606(4)</td>
<td>127</td>
<td>S(6)</td>
<td></td>
</tr>
<tr>
<td>N1b—H1...O2</td>
<td>0.86</td>
<td>2.56</td>
<td>3.366(4)</td>
<td>156</td>
<td>1-x, 1-y, 2-z</td>
<td>R$_2^{(12)}$</td>
</tr>
<tr>
<td>C1b—H1b...O2</td>
<td>0.93</td>
<td>2.54</td>
<td>3.422(5)</td>
<td>158</td>
<td>1-x, 1-y, 2-z</td>
<td>R$_2^{(6)}$</td>
</tr>
<tr>
<td>C6—H6...N2b</td>
<td>0.93</td>
<td>2.38</td>
<td>2.712(5)</td>
<td>101</td>
<td>S(5)</td>
<td></td>
</tr>
<tr>
<td><strong>Short Contacts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y—X...Cg</td>
<td></td>
<td></td>
<td>1.237(4)</td>
<td>3.410(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y...Cg</td>
<td></td>
<td></td>
<td>3.757(4)</td>
<td>96.5(2)</td>
<td>x, 1+y, z</td>
<td></td>
</tr>
</tbody>
</table>

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$_2^{(12)}$ (12) rings. Meanwhile pairs of the C1b—H1b...O2 hydrogen bond [2.55 Å, 157 °], generates R$_2^{(6)}$ (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(I) 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 Yeifar.

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

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

π interactions between the two aryl groups, such an interaction is absent in compound I.

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

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 Yeifar, there are π-

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 953347 contains 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).

References


