

Synthesis, Characterization and Crystal Structure of *trans*-2-(2-Hydroxyphenyl)-1-nitroethylene

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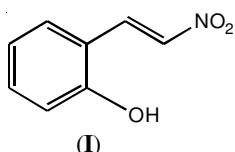
The nitroalkene compound, namely *trans*-2-(2-hydroxyphenyl)-1-nitroethylene (**I**), has been successfully synthesized from the condensation of 2-hydroxybenzaldehyde with nitromethane. It was characterized by elemental analysis, ¹H NMR spectrum and single-crystal X-ray diffraction analysis. Compound (**I**) crystallizes in the triclinic, space group P-1 with *a* = 5.2270(5), *b* = 11.2130(10), *c* = 13.6080(13) Å, α = 71.224(18), β = 84.47(3), γ = 81.20(3)°, *V* = 745.29(16) Å³, *Z* = 4, C₈H₇NO₃, *M_r* = 165.15, *D_c* = 1.472 g/cm³, *F*(000) = 344, μ (MoK α) = 0.115 mm⁻¹, the final *R*₁ = 0.0500 and *wR*₂ = 0.1358 for 2309 observed reflections [*I* > 2 σ (*I*)]. Moreover, the crystal structure of (**I**) is stabilized by the intermolecular O-H...O hydrogen bonds, the π - π stacking interactions and the C-H...O short contacts, which extend the molecules into an infinite three-dimensional network.

Keywords: Nitroalkene, Synthesis, Crystal Structure, Intermolecular interaction.

INTRODUCTION

The nitroalkene compounds have attracted much attention from a synthetic point of view because they are recognized as one of the most valuable building blocks in the organic synthesis. For example, the nitro functionality with the multiple reactivity undergoes conversion to 1,3-dipoles, oxidation to carboxylic acids and reduction to hydroxylamines¹⁻³; furthermore, the C=C double bond activated by the nitro group reacts with various nucleophiles by means of Michael addition reaction⁴⁻⁶. Meanwhile, the nitroalkenes and their derivatives display diverse biological activities such as insecticidal activities, anticancer activities and anti-HVI-1 activities⁷⁻⁹, etc. For better understanding of the relationship between molecular structures and biological activities, the detailed investigation on the synthesis and structures of such compounds seems very important.

In continuation of the study on such important compounds¹⁰⁻¹³, we herein report the synthesis, characterization and crystal structure of a nitroalkene compound, namely *trans*-2-(2-hydroxyphenyl)-1-nitroethylene (**I**) (**Scheme-I**).



Scheme-I

EXPERIMENTAL

All the chemicals were of reagent grade and used without further purification. Melting points were determined on a YRT-3 apparatus and are uncorrected. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 240 C analyzer. ¹H NMR spectrum was obtained on a Bruker AV-400 instrument (400 MHz) using TMS as an internal standard and CDCl₃ as solvent.

Synthetic procedure: 2-Hydroxybenzaldehyde (1.22 g, 10 mmol), nitromethane (1.36 mL, 25 mmol) and methanol (4.20 mL) are added to a three-neck round bottomed flask and cooled to 0 °C. While maintaining the internal reaction temperature between 0-15 °C, aqueous 1 M NaOH (25 mL, 25 mmol) is added by an addition funnel and the mixture is stirred for 15 min. Ice water mixture (17.50 mL) is added and the reaction is stirred at 0 °C for 0.5 h. The reaction mixture is slowly added to aqueous 8M HCl (16.80 mL, 134 mmol) and allowed to stir until the reaction is confirmed complete by TLC. After the reaction mixture is filtered and recrystallized from ethanol, the title compound (**I**) was afforded as the brown-red solid (0.71 g, yield of 43 %). m.p.: 134-135 °C. Anal. Calcd. (%) for C₈H₇NO₃: C, 58.18, H, 4.27, N, 8.48. Found (%): C, 58.27, H, 4.38, N, 8.35. ¹H NMR (400 MHz, CDCl₃, TMS) δ /ppm: 8.14 (d, *J* = 13.6 Hz, 1H, =CH-a), 7.96 (d, *J* = 13.6 Hz, 1H, =CH-b), 7.44 (d, *J* = 7.2 Hz, 1H, PhH-c), 7.36 (t, *J* = 7.2 Hz, 1H, PhH-e), 7.02 (t, *J* = 7.2 Hz,

1H, *PhH*-d), 6.86 (d, $J = 7.2$ Hz, 1H, *PhH*-f), 5.61 (s, 1H, *OH*-g).

Crystal structure determination: Single crystals of the title compound (**I**) suitable for X-ray diffraction analysis were grown by slow evaporation of the acetonitrile/hexane solution at 5 °C. The single crystal with dimensions of $0.28 \times 0.26 \times 0.12$ mm for (**I**) was mounted on a Rigaku Saturn CCD area detector. Data were collected at 113(2) K for (**I**) by using a graphite monochromator with $\text{MoK}\alpha$ radiation ($\lambda = 0.71075$ Å). A total of 6966 reflections were collected in the range of $1.583^\circ \leq \theta \leq 27.874^\circ$ by using an the ω - ϕ scanning mode, of which 3445 were unique with $R_{\text{int}} = 0.0521$ and 2309 were observed with $I > 2\sigma(I)$. The structures were solved by direct methods using the SHELXS-97 program¹⁴ and refined by full-matrix least-squares techniques (SHELXL-97)¹⁵ on F^2 . Hydrogen atoms were located by using the geometric method. The final $R = 0.0500$, $wR = 0.1358$ ($w = 1/[\sigma^2(F_o)^2 + (0.0678P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 0.97$, $(\Delta/\sigma)_{\text{max}} = 0.001$, $(\Delta\rho)_{\text{max}} = 0.272$ and $(\Delta\rho)_{\text{min}} = -0.288$ e/Å³. 3445 ($R_{\text{int}} = 0.0521$).

RESULTS AND DISCUSSION

The elemental analyses of the title compound (**I**) are in good agreement with the supposed compositions of $\text{C}_8\text{H}_7\text{NO}_3$. The ¹H NMR data of (**I**) are well attributed as displayed in Fig. 1.

Structure of the title compound (I**):** The single crystal of the title compound (**I**) was obtained by slow diffusion of *n*-hexane to the acetonitrile solution of (**I**), which was crystallized as air-stable brown-red crystals. Crystallographic and refinement parameters are listed in Table-1. The selected bond lengths and angles are given in Tables-2 and 3, respectively.

The molecular structure of (**I**) is depicted in Fig. 2. The crystal packing diagram of (**I**) is shown in Fig. 3.

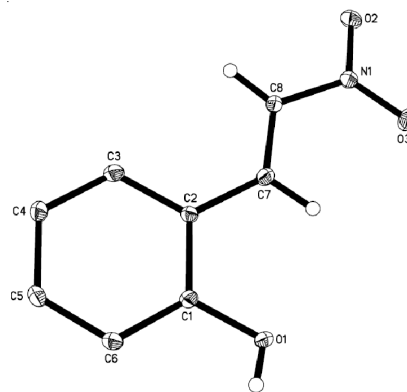


Fig. 2. Molecular structure of (**I**) with 30 % probability thermal ellipsoids

As depicted in Fig. 2, the title compound (**I**) displays a *trans* configuration about the C=C double bond. The average

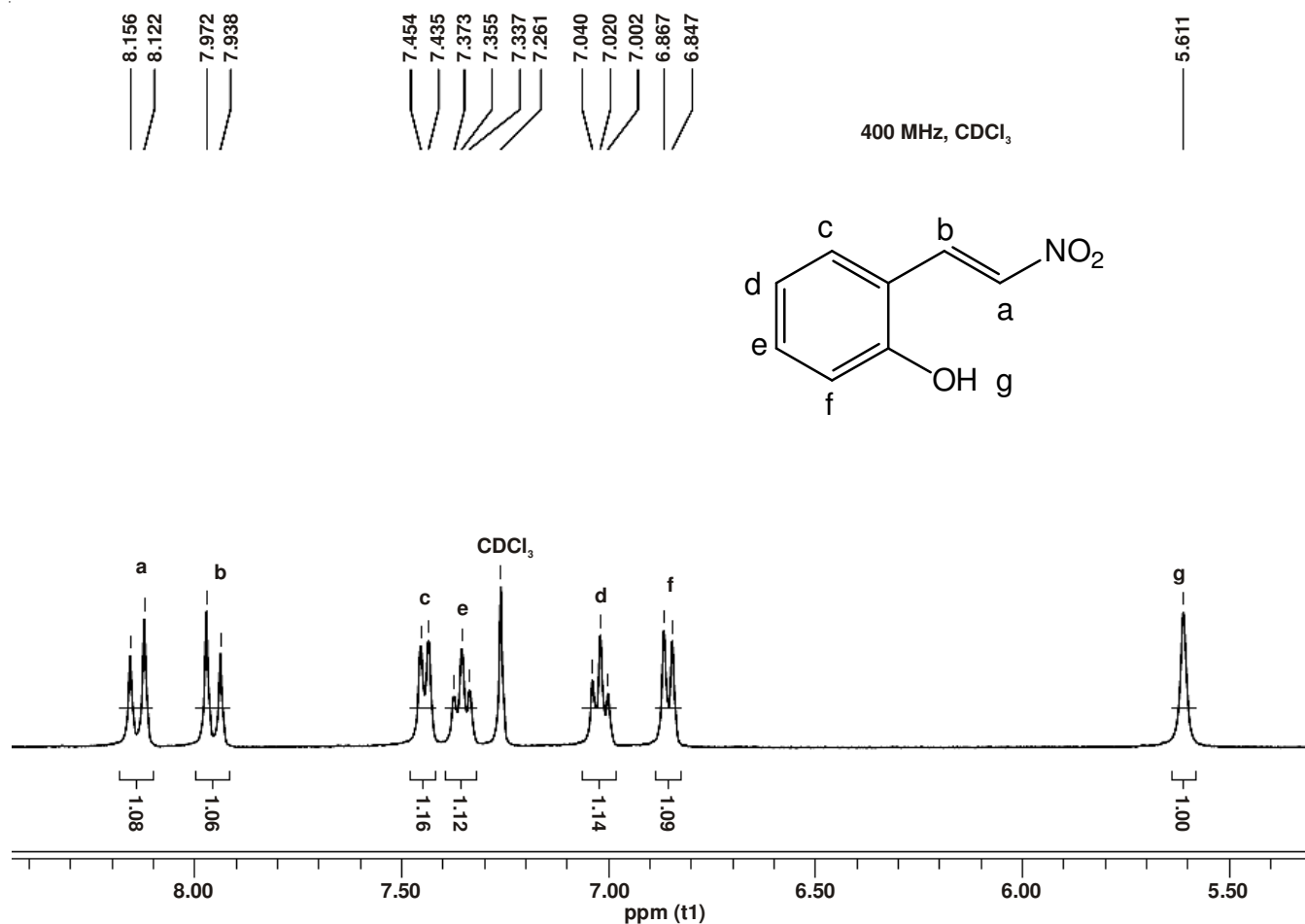
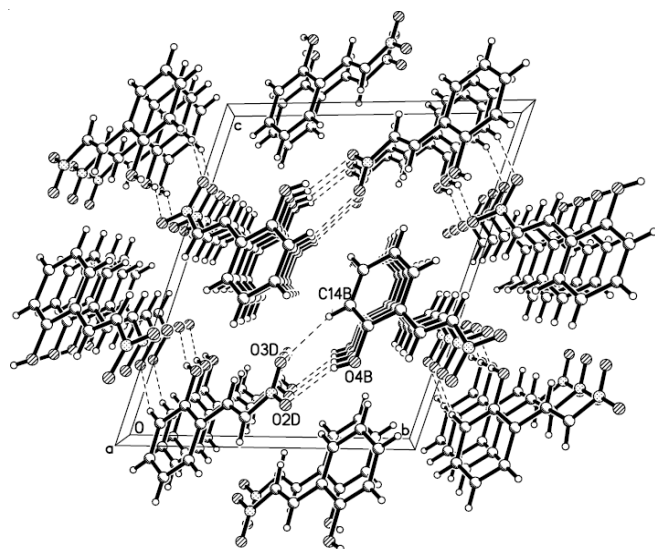


Fig. 1. ¹H NMR spectrum of (**I**)

Fig. 3. Crystal packing diagram of (I) along the a -axis

bond lengths and angles (Table-2 and 3) are in agreement with those observed in the previously reported nitroethylenes¹⁰⁻¹³. The C(7)=C(8) bond length (1.336(2) Å) is close to the isolated C=C bond (1.337 Å)¹⁶, conforming it is a typical double bond. The C(8)-N(1) bond length (1.429(2) Å) and the C(2)-C(7) one (1.448(2) Å) is shorter than the normal C-N single bond (1.47 Å)¹⁷ and the normal C-C single bond (1.46 Å)¹⁸, respectively, indicating that C(7)=C(8) double bond are simultaneously

TABLE-1
CRYSTAL DATA AND STRUCTURAL REFINEMENT FOR (I)

Parameters	Values
Empirical formula	C ₈ H ₇ NO ₃
Formula weight	165.15
Crystal system	Triclinic
Unit cell dimensions	
a (Å, °)	5.2270(5)
b (Å, °)	11.2130(10)
c (Å, °)	13.6080(13)
Unit cell angles (°)	
α	71.224(18)
β	84.47(3)
γ	81.20(3)
Volume (Å ³)	745.29(16)
Z	4
Temperature (K)	113(2)
Space group	P-1
Wavelength (Å)	0.71075
Calculated density (g cm ⁻³)	1.472
Absorption coefficient μ (mm ⁻¹)	0.115
F(000)	344
Crystal size (mm ³)	0.280 x 0.260 x 0.120
θ range for data collection (°)	1.583 - 27.874
Limiting indices	-6 $\leq h \leq$ 6, -14 $\leq k \leq$ 14, -17 $\leq l \leq$ 17
Reflection collected	6966
Independent reflection	3445 ($R_{int} = 0.0521$)
Completeness to θ_{max} (%)	98.3
Data/restraints/parameters	3445/0/225
Goodness-of-fit on F^2	0.970
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0500$, $wR_2 = 0.1283$
R indices (all data)	$R_1 = 0.0674$, $wR_2 = 0.1358$
Largest diff.e peak and hole (e Å ⁻³)	0.272 and -0.288

TABLE-2
SELECTED BOND LENGTHS (Å) FOR (I)

Bonds	Dist.
O(2)-N(1)	1.2409(19)
O(3)-N(1)	1.2248(18)
N(1)-C(8)	1.429(2)
C(7)-C(8)	1.336(2)
C(2)-C(7)	1.448(2)
O(1)-C(1)	1.366(2)

TABLE-3
SELECTED BOND ANGLES (°) FOR (I)

Angles	(°)
O(3)-N(1)-O(2)	121.97(15)
O(3)-N(1)-C(8)	120.52(15)
O(2)-N(1)-C(8)	117.51(14)
C(3)-C(2)-C(1)	117.98(16)
C(3)-C(2)-C(7)	123.17(15)
C(1)-C(2)-C(7)	118.85(15)
C(8)-C(7)-C(2)	126.46(16)
C(7)-C(8)-N(1)	119.51(15)
O(1)-C(1)-C(2)	117.45(16)

conjugated with the benzene ring and the nitro group¹⁷. Furthermore, the dihedral angle between the C(7)/C(8)/N(1)/O(1)/O(2) plane (r.m.s deviation 0.0388 Å) and the C(1)-C(6) plane (r.m.s. deviation 0.0048 Å) is 4.1°, which suggests that the nitroethylene unit is well planar with the 2-hydroxyphenyl moiety. This is because that the significant level of π -electron delocalization in the molecular system leads to the planarity of the molecule¹⁹. In addition, the C(7)-C(8)-N(1) bond angle (119.51(15)°) is shorter than the C(8)-C(7)-C(2) bond angle (126.46(16)°), probably due to the intramolecular C-H...O hydrogen bond between the hydrogen atom of the ethylene moiety and the oxygen atom of the hydroxyl group.

As shown in Fig. 3, the title molecules are stabilized by the three kinds of intermolecular interactions as follows: (i) the intermolecular O-H...O hydrogen bonds between the H atoms of the hydroxyl group with the O atoms of the nitro group are observed in adjacent molecules, in which the bond length is 2.191 Å; (ii) there are π - π stacking interactions involving the benzene rings of two adjacent molecules, where the two rings are parallel to each other with the centroid-to-centroid separation of 4.308 Å. (iii) the C-H...O short contacts between the H atom of the benzene ring and the O atom of the nitro group exist in adjacent molecules^{19,20}, in which the distance is 2.455 Å; Consequently, these intermolecular interactions extend the nitroethylene molecules into an infinite three-dimensional network.

Conclusion

In summary, the nitroalkene compound [*trans*-2-(2-hydroxyphenyl)-1-nitroethylene (I)] has been synthesized and structurally characterized elemental analysis and ¹H NMR spectrum. Particularly, the molecular structure of (I) was unequivocally determined by single-crystal X-ray diffraction analysis, in which the C=C double bond is in a *trans* configuration in the solid state. In addition, there are intermolecular O-H...O hydrogen bonds, π - π stacking interactions and C-H...O short contacts in the crystal structure of (I), which link the title molecules into an infinite three-dimensional network.

Supplementary data: CCDC-960452 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; or E-mail: deposit@ccdc.cam.ac.uk).

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