

(E)-2-acetyl-4-(4-methoxyphenyldiazenyl) phenol: X-ray and DFT-calculated structure

Serap YAZICI^{1,*}, Çiğdem ALBAYRAK², İsmail Erdem GÜMRÜKÇÜOĞLU³,
İsmet ŞENEL¹, Orhan BÜYÜKGÜNGÖR¹

¹*Physics Program, Faculty of Arts & Sciences, Ondokuz Mayıs University,
Samsun, 55139, TURKEY
e-mail: yserap@omu.edu.tr*

²*Faculty of Education, Sinop University, Sinop, 57100, TURKEY*

³*Chemistry Program, Faculty of Arts & Sciences, Ondokuz Mayıs University,
Samsun, 55139, TURKEY*

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The crystal structure of the title compound, (E)-2-acetyl-4-(4-methoxyphenyldiazenyl) phenol, displays a trans configuration of the azo moiety as found for other azo (diazene) derivatives. The aromatic mean planes are nearly coplanar and the dihedral angle between the 2 aromatic rings is 3.04(8)°. The molecules, with strong intramolecular O–H...O hydrogen bonding, are linked by weak van der Waals interactions in the 3-dimensional network. The molecular geometry, determined using X-ray diffraction techniques, was also calculated with the density functional theory (DFT), employing the hybrid exchange-correlation functional B3LYP. Experimental and theoretical IR spectra of the compound were also calculated for comparison. The results of the experimental and theoretical calculations are compared in this study.

Key Words: Diazenyl, X-ray, IR, DFT

Introduction

Aromatic azo compounds represent the dominant class of synthetic colorants. Azo compounds have long been used in industry because of their versatile applications in various fields and high technology areas, including dyes for textile fibers, colorings for different materials, plastics, biological and medical studies, lasers, liquid crystalline displays, electrooptical devices, and inkjet printers.¹ The reversible interconversion of the cis and trans isomers of azo compounds allows the use of these compounds in optical data storage and switching

*Corresponding author

(E)-2-acetyl-4-(4-methoxyphenyldiazenyl) phenol:..., *S. YAZICI, et al.*,

devices.^{2,3} Such optical properties depend not only on the spectroscopic properties of the molecules, but also on their crystallographic arrangement.⁴ Related to uses of azo compounds, we present here the crystal and molecular structure of the title compound.

Experimental

Synthesis

A mixture of 4-methoxyaniline (0.96 g, 7.8 mmol), water (20 mL), and concentrated hydrochloric acid (1.97 mL, 23.4 mmol) was stirred until a clear solution was obtained. This solution was cooled to 273-278 K and a solution of sodium nitrite (0.75 g, 7.8 mmol) in water was added dropwise while the temperature was maintained below 278 K. The resulting mixture was stirred for 30 min in an ice bath. A 2-hydroxyacetophenone (1.067 g, 7.8 mmol) solution (pH 9) was gradually added to a cooled solution of 4-methoxybenzenediazonium chloride, prepared as described above, and the resulting mixture was stirred at 273-278 K for 60 min in an ice bath. The product was recrystallized from ethyl alcohol to obtain solid (E)-2-acetyl-4-(4-methoxyphenyldiazenyl) phenol. Crystals of (E)-2-acetyl-4-(4-methoxyphenyldiazenyl) phenol were obtained after 2 days by slow evaporation from acetic acid (yield 67%, mp 127-128 °C). The IR spectrum was recorded in the 4000-400 cm⁻¹ region with a Bruker Vertex 80V FT-IR spectrometer using KBr pellets.

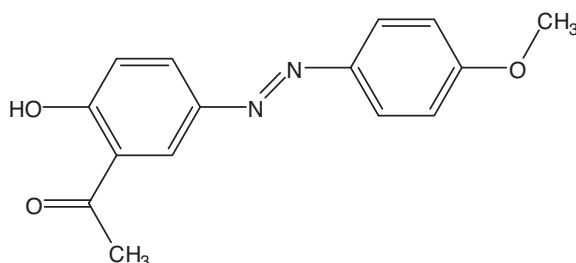


Figure 1. The chemical structure of the title compound.

X-Ray diffraction analysis

A suitable sample of size $0.69 \times 0.42 \times 0.24$ mm³ was selected for the single crystal X-ray study. All diffraction measurements were performed at a low temperature (150 K) using graphite-monochromated Mo K α radiation and a STOE IPDS 2 diffractometer. Reflections were collected in the rotation mode and cell parameters were determined by using X-AREA software.⁵ Absorption correction was achieved by the integration method via X-RED software.⁵ The structure was solved by direct methods using SHELXS-97.⁶ The refinement was carried out by the full-matrix least-squares method using SHELXL-97⁶ on the positional and anisotropic temperature parameters of the nonhydrogen atoms, equivalently corresponding to 185 crystallographic parameters. All nonhydrogen atom parameters were refined anisotropically and all H atoms, except for H1, were located in their idealized positions and refined using a riding model, fixing the aromatic C-H distances at 0.93 Å, the methyl C-H distances at 0.96 Å, the O-H distance at 0.95 Å, and the $U_{iso}(H)$ values in the range of 1.2 $U_{eq}(C)$ or 1.5 $U_{eq}(C)$. The data collection conditions and parameters of the refinement process are listed in Table 1.

Table 1. Crystal data, data collection, and refinement details.

Chemical formula	C ₁₅ H ₁₄ N ₂ O ₃
Formula weight	270.28
Crystal system	Triclinic
Space group	<i>P</i> – 1
Z	2
a, b, c	6.7909(4), 8.9765(5), 11.3727(6) Å
$\alpha\beta, \gamma$	88.751(4), 73.213(4), 79.056(4) ^o
V	651.25(6) Å ³
D _x	1.378 mg m ⁻³
Radiation, λ	Mo K α , 0.71073 Å
M	0.098 mm ⁻¹
T	150 K
T _{min} , T _{max}	0.953, 0.98
Scanning mode	ω scan
Scan range	-8 < h < 8, -11 < k < 11, -14 < l < 14
Crystal size	0.69 × 0.42 × 0.24 mm
$\theta_{min}, \theta_{max}$	1.87 ^o , 2799 ^o
Number of measured/independent reflections, R _{int}	10487/2562, 0.061
Number of reflections with I > 2 σ (I)	2173
Number of refined parameters	185
S	1.08
R[F ² > 2 σ (F ²)]	0.43
wR(F ²)	0.127
$\Delta\rho_{max}, \Delta\rho_{min}$	0.25, -0.22 e Å ⁻³

Computational procedure

Full geometry optimization of the isolated molecule was calculated using the DFT-B3LYP hybrid exchange-correlation functional with the 6-31G(d,p) basis set.^{7,8} For the calculations, the starting geometry was taken from the final X-ray refinement cycle of the molecule. In this study, all theoretical calculations were performed by means of the GAUSSIAN 03W package.⁹ Optimized molecular geometry, total molecular energy, dipole moment, Mulliken charges, theoretical IR spectra, and the molecular orbital descriptions HOMO and LUMO for the title compound were obtained from the computational calculations.

Results and discussion

An ORTEP¹⁰ view of the molecular structure of the title compound is shown in Figure 2 with the atom numbering scheme. The N1–C1 and N2–C9 bond lengths of 1.421(1) and 1.418(1) Å by X-ray and 1.4113 and

1.4103 Å by DFT, respectively, indicate a single-bond character, and the N1=N2 bond lengths of 1.262(1) Å for X-ray and 1.2644 Å for DFT are indicative of a significant double-bond character. These values are consistent with those for similar compounds.^{11–14} The C7–O2 bond distance in (I) was 1.238(1) Å by X-ray and 1.2419 Å by B3LYP/6–31G(d,p), consistent with the value of the C=O double bond in carbonyl compounds.¹⁵

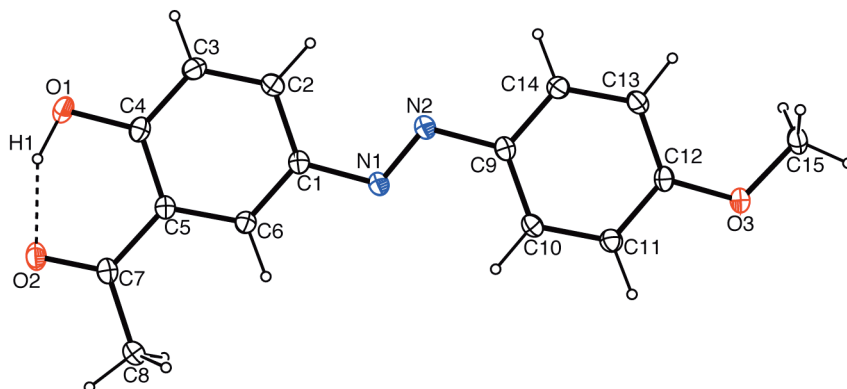


Figure 2. An ORTEP-3 view of the title compound with the atomic numbering scheme. Dashed line shows an intramolecular hydrogen bond. Displacement ellipsoids are shown at the 30% probability level.

In order to investigate the aromaticity of the rings, HOMA (harmonic oscillator model of aromaticity) indices were calculated for the compound.^{16,17} The HOMA index is equal to 1 for aromatic systems and 0 for nonaromatics. The calculated indices were 0.938 for the hydroxyl-group-attached ring and 0.974 for the methoxy-attached ring. These values also indicate that the investigated molecule consists of 2 aromatic rings. The aromatic rings linked through a diazene bridge are in a trans configuration with respect to the azo double bond. The title molecule is almost coplanar and the dihedral angle between the planes is 3.04(8)° and 0.0118° by X-ray and B3LYP/6–31G(d,p), respectively.

As can be seen in Figure 2, atom H1 bonded to O1 forms a strong intramolecular hydrogen bond with atom O2 [$D \dots A = 2.553(1)$ Å]. The sum of the van der Waals radii of the O and O atoms (3.04 Å) is significantly longer than the intramolecular O...O hydrogen bond length.¹⁸ The crystal packing is stabilized by weak van der Waals forces.

Table 2. Hydrogen bonding geometry (Å, °).

D–H...A	D–H	H...A	D...A	∠D–H...A
O1–H1...O2	0.95(2)	1.67(2)	2.553(1)	153(2)

Some selected geometric parameters experimentally obtained and theoretically calculated by B3LYP/6–31G(d,p) are listed in Table 3. C1–N1–N2–C9, C2–C1–N1–N2 and C10–C9–N2–N1 torsion angles, which determine molecular geometry, were -9.3(1)°, 5.7(1)°, and -179.95(8)° by X-ray and 0.0172°, -0.0057°, and 179.9957° by B3LYP geometries, respectively. As can be seen from Table 3, between the calculated and observed geometrical parameters, there were some differences. Since the experimental results were obtained from molecules in the solid state while the theoretical results were based on an isolated molecule in the gaseous phase, these differences were not unforeseen.

Table 3. Selected bond lengths, angles, and torsion angles (\AA , $^\circ$).

	X-ray	DFT/B3LYP
N1–N2	1.262(1)	1.2644
C9–N2	1.418(1)	1.4103
C1–N1	1.421(1)	1.4113
C4–O1	1.346(1)	1.3337
C12–O3	1.364(1)	1.3602
C7–O2	1.238(1)	1.2419
O1–C4–C3	117.3(1)	118.1284
C12–O3–C15	117.6(1)	118.4284
C10–C9–N2–N1	-9.3(1)	0.0172
C2–C1–N1–N2	5.7 (1)	-0.0057
C1–N1–N2–C9	-179.95(8)	179.9957
C4–C5–C7–O2	-1.9(1)	-0.0054

In the DFT-B3LYP calculations of the isolated molecule, the total energy was obtained as $-3989.9982 \times 10^{-18}$ J. The Mulliken charges¹⁹ of the atoms were also calculated for the compound. All oxygen and nitrogen atoms had more negative charges than the other atoms in the molecule. The charges of the O1, O2, and O3 atoms were -0.553, 0.523, and -0.512, respectively, and the charges of the N1 and N2 atoms were -0.322 and -0.320, respectively, as expected. Due to this charge distribution, the dipole moment of the molecule becomes 4.1744 D.

The theoretical calculations indicate that the title compound has 71 occupied molecular orbitals (MO). According to the MO calculations for the compound, the energy gap between the HOMO and LUMO is 3.59 eV. Since the HOMO-LUMO energy separation has been used as a simple indicator of kinetic stability in previous studies,^{20,21} this large energy gap indicates that the title compound should be quite stable.

The theoretical frequencies of the molecule, scaled by 0.9627,²² are given in Table 4 in comparison with the experimental results. While the experimental C=O and N=N stretching modes were observed at 1639 and

Table 4. The experimental and calculated frequencies of IR spectra (cm^{-1}).

Assignments	Experimental	DFT/B3LYP
O–H str.	2000-3000	3101
C=O str.	1639	1645
N=N str.	1423	1479
C–O str. (aromatic)	1243	1291
C–O str. (aromatic)	1215	1248
C–C str. (aromatic)	1600-1580	1599-1561
O–H bend.	1327	1388

Str.: stretching, bend.: bending.

(E)-2-acetyl-4-(4-methoxyphenyldiazenyl) phenol:..., *S. YAZICI, et al.*,

1423 cm⁻¹, respectively, the theoretical stretching modes were achieved at 1645 and 1479 cm⁻¹, respectively. The above conclusions are in good agreement with the literature values.^{23,24} Because of the participation of the carbonyl group in hydrogen bonding, the experimental frequencies were found to be significantly lower than the theoretical values. Due to the same reason, the O-H stretching band was experimentally located at about 2000-3000cm⁻¹.²⁵

Supplementary data

CCDC 747871 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033.

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