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2,6-Dimethyl-1,4-benzoquinone 4-monooxime

Mustafa Odabaşoğlu,[a] Çiğdem Albayrak[a] and Orhan Büyükgüngör[b]*

[a]Department of Chemistry, Ondokuz Mayıs University, TR-55139 Samsun, Turkey, and [b]Department of Physics, Ondokuz Mayıs University, TR-55139 Samsun, Turkey
Correspondence e-mail: orhanb@omu.edu.tr

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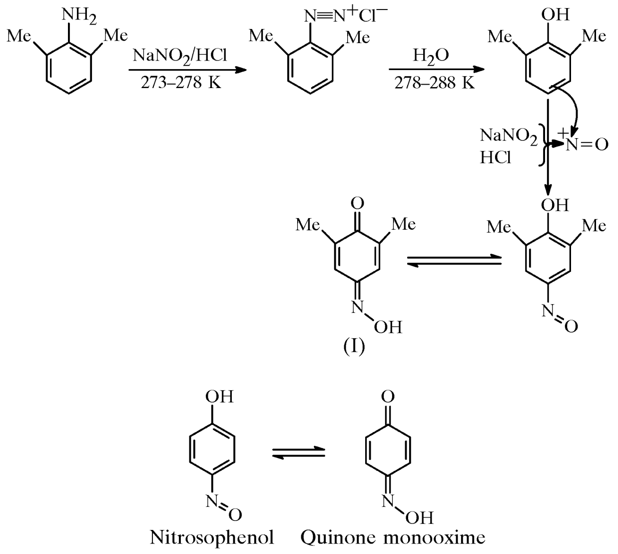
Molecules of the title compound, $C_8H_9NO_2$, are linked into sheets by a combination of C—H···N, O—H···N and O—H···O hydrogen bonds and C—H···π interactions. The hydrogen bonds are arranged as described by the graph-set ring notations $R_2^2(7)$ and $R_3^3(5)$, and a $C8$ chain motif. There are two planar symmetry-independent molecules in the asymmetric unit, with a dihedral angle of 19.24 (5)° between their least-squares mean planes.

Comment

H-atom transfer in a hydrogen bond is an elementary process present in many systems of biological interest. Recently, many experimental and computational studies have addressed H-atom dynamics in hydrogen bonds (Yan *et al.*, 2001; Mavri & Grdadolnik, 2001*a*,*b*; Rospenk *et al.*, 2001; Došlći *et al.*, 2001). In addition, the quinone monooximate (nitroso) complexes of transition metals are of interest in respect of their structure, reactivity and possible application as starting reagents in the synthesis of a wide variety of organic compounds (Kasumov *et al.*, 2000). Quinone monooxime compounds are an example of systems possessing both intra- and intermolecular hydrogen bonds (Kržan & Mavri, 2002). They are key reagents in the production of azo dyes. Since they are good complexing agents, they have found a place in many analytical, synthetic and other applications (Carugo *et al.*, 1991; Shipmen *et al.*, 1955; Castellani & Millini, 1984; Verdoorn *et al.*, 1994). In solution, quinone monooximes generally exist as a mixture of quinone monooxime–nitrosophenol and –nitrosonaphthol tautomers (see scheme).

The nitroso–oxime tautomeric equilibrium has been extensively studied by spectroscopic methods, including UV, IR and NMR techniques (Fischer *et al.*, 1965; Enchev *et al.*, 1999; Ivanova & Enchev, 2001). The latter is a particularly powerful method for studying the structure and dynamics of such hydrogen-bonded systems (Abilgaard *et al.*, 1998). In the classic study on nitrosophenols (Burawoy *et al.*, 1955), it was shown that, in solution, 2-nitrosophenol exists exclusively in the phenolic form, while the 5-methoxy and 5-dimethylamino derivatives are found in solvent-dependent equilibrium with their corresponding quinonoid forms. In general, it was established that quinonoid forms are favoured in polar solvents, while phenolic forms are favoured in non-polar solvents (Kržan *et al.*, 2000). Generally, *o*-nitrosophenols exist in the quinone monooxime form, while *p*-nitrosophenols exist in the nitrosophenol form (Abilgaard *et al.*, 1998; Kržan *et al.*, 2000; Kržan & Mavri, 2002). As we could not find in the literature any example of a solid-state compound in the quinone monooxime form, an X-ray structure determination of the title compound, (I), was carried out and the results are presented here.



2,6-Dimethyl-1,4-benzoquinone monooxime, (I), was synthesized according to the reaction mechanism in the scheme. In the structure of (I), there are two symmetry-independent molecules in the asymmetric unit (Fig. 1). Selected bond distances and angles (I) are listed in Table 1. Compound (I) possesses normal geometrical parameters and,

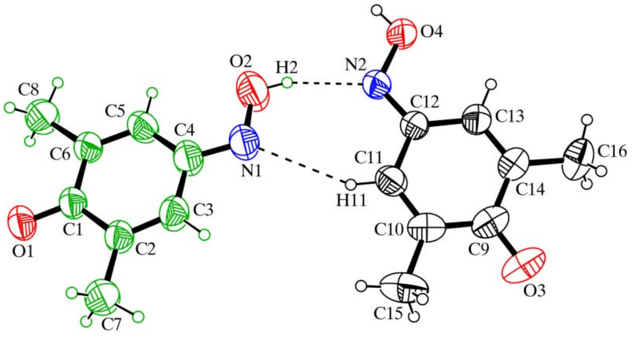


Figure 1
A view of the two independent molecules of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the intermolecular hydrogen bonds.

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as expected, is essentially planar [for the non-H atoms, the largest r.m.s. deviations from the best least-squares plane are −0.008 (2) Å for the C1–C6 ring and 0.024 (2) Å for the C9–C14 ring].

The present determination reveals that compound (I) exists as the quinone–oxime tautomer in the solid state. This is evident from the relative contraction of the C1—O1, C4—N1, C2—C3 and C5—C6 bonds, and the relative elongation of the C1—C2, C3—C4, C4—C5, C1—C6 and N1—O2 bonds. A similar pattern of bond contractions and elongations was also observed for the C9–C14 ring (Table 1). It should be noted here that the tautomers of *o*-benzoquinone monoxime have been investigated by Carugo *et al.* (1991). The N—O bond distances in the *o*-benzoquinone monoxime and its nitrosophenol tautomer are reported to be 1.378 and 1.200 Å, respectively. The corresponding values in (I) are 1.362 (3) Å for N1—O2 and 1.377 (2) Å for N2—O4, showing that both molecules are in the quinone monooxime form. The orientations of the methyl groups are thought to be determined by the steric effects of the adjacent carbonyl groups. All the non-H atoms in each molecule lie in the same plane, as shown by the r.m.s. deviations of 0.003 (2) and 0.003 (2) Å from the corresponding least-squares mean planes.

Further examination of non-bonded contacts also reveals four intermolecular hydrogen bonds (Table 2). Hence, as shown in Fig. 1, asymmetric units of (I) are linked through C11—H11···N1 and O2—H2···N2 hydrogen bonds, and the dihedral angle between the C1–C6 and C9–C14 rings is 19.24 (5)°. The arrangement of the C11—H11···N1 and O2—H2···N2 hydrogen bonds can be described by the graph-set notation $R_2^2(7)$. Other hydrogen bonds are arranged as described by $R_3^3(5)$ and a *C*8 chain motif in the *bc* plane (Fig. 2) (Bernstein *et al.*, 1995).

Stacking of the quinoid rings in (I) shows a $Cg1\cdots Cg1^{i}$ separation of 3.6375 (14) Å [*Cg*1 is the centroid of the C1–C6 ring; symmetry code: (i) $\frac{1}{2}+x, y, \frac{1}{2}-z$].

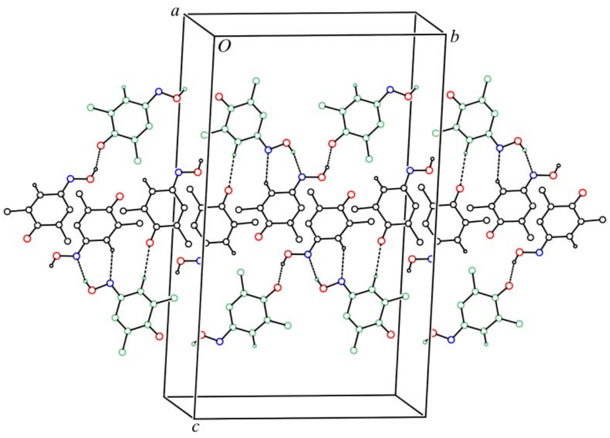

Figure 2
A view of packing diagram of (I) along the *a* axis. Hydrogen bonds are shown as dashed lines.

Experimental

A mixture of 2,6-dimethylaniline (1.51 g, 10 mmol), water (50 ml) and concentrated hydrochloric acid (2.5 ml, 30 mmol) was heated with stirring until a clear solution was obtained. This solution was cooled to 273–278 K and a solution of sodium nitrite (0.96 g, 14 mmol) in water was added dropwise. The resulting mixture was stirred for 30 min at 278–288 K. The precipitated product was crystallized from acetonitrile to obtain crystals of 2,6-dimethyl-1,4-benzoquinone monooxime, (I) (m.p. 444–446 K).

Crystal data

$C_8H_9NO_2$
$M_r = 151.16$
Orthorhombic, *Pbca*
$a = 7.2505\ (7)$ Å
$b = 16.3379\ (10)$ Å
$c = 26.4894\ (17)$ Å
$V = 3137.9\ (4)$ Å^3
$Z = 16$
$D_x = 1.280$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 7762 reflections
$\theta = 1.5$–$25.9°$
$\mu = 0.09$ mm^{-1}
$T = 296$ K
Tetragonal prism, red
0.30 × 0.17 × 0.09 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
20 873 measured reflections
3089 independent reflections
1718 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.062$
$\theta_{\rm max} = 26.1°$
$h = -8 \rightarrow 8$
$k = -17 \rightarrow 20$
$l = -32 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.143$
$S = 0.87$
3089 reflections
198 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0913P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0052 (11)

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.238 (2)	C9—C10	1.470 (3)
C1—C6	1.466 (3)	C9—C14	1.480 (3)
C1—C2	1.469 (3)	C10—C11	1.336 (3)
C2—C3	1.331 (3)	C11—C12	1.448 (3)
C3—C4	1.430 (3)	C12—N2	1.297 (2)
C4—N1	1.320 (3)	C12—C13	1.443 (3)
C4—C5	1.440 (3)	C13—C14	1.338 (3)
C5—C6	1.343 (3)	N1—O2	1.362 (3)
C9—O3	1.231 (3)	N2—O4	1.377 (2)
C4—N1—O2	110.74 (18)	C12—N2—O4	112.90 (16)
C3—C4—N1—O2	179.1 (2)	C13—C12—N2—O4	−1.1 (3)
C5—C4—N1—O2	0.6 (4)	C11—C12—N2—O4	178.28 (19)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N2	0.82	2.06	2.862 (2)	164
O4—H4···O1^{i}	0.82	1.84	2.643 (2)	164
C3—H3···O3^{ii}	0.93	2.58	3.432 (3)	153
C11—H11···N1	0.93	2.61	3.453 (3)	152

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

Methyl H atoms were located from difference Fourier syntheses and refined as part of a rigid rotating group, with C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C). Other H atoms were placed geometrically and refined using a riding model, with Csp^2—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1603). Services for accessing these data are described at the back of the journal.

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