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SHORT COMMUNICATION

CRYSTAL STRUCTURE OF 2-(3,5-DIMETHOXYPHENYLAMINO)-3-CHLORONAPHTHALENE-1,4-DIONE

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ABSTRACT. 2-(3,5-Dimethoxyphenylamino)-3-chloronaphthalene-1,4-dione compound was prepared from the nucleophilic substitution reaction of 2,3-dichloro-1,4-naphthoquinone with 3,5-dimethoxyphenylamine at reflux temperature according to literature reported previously. Single-crystal X-ray diffraction analysis was carried out to confirm the structure of the title compound. The title compound, $C_{18}H_{14}ClNO_4$, crystallizes in the triclinic space group P-1, a = 7.0016(6) Å, b = 7.7937(6) Å, c = 15.6218(11) Å, β = 97.238(4)°, V = 782.44(11) Å^3, Z = 2, R_1 = 0.0525, wR_2 = 0.1329.

KEY WORDS: Naphthoquinones, Aminochloronaphthoquinone; X-Ray diffraction

INTRODUCTION

Synthetic naphthoquinone compounds containing a variety of substituents such as chloro, thio, amino, arylamino are increasingly finding applications in many areas, especially related to textile [1], pharmaceutical [2], agrochemical [3], and drug industries [4]. Dyes are also very important materials [5, 6] that most quinones found themselves in [7]. They also display reach biological activities [8] like antifungal [9], antibacterial [10], anticancer [11], antimalarial [12], hypoglycemic [13], analgesic [14], anti-inflammatory [15], and HIV inhibitory [16]. The redox polymers based on quinones owing to their redox ability have been investigated to develop batteries and biosensors [17, 18]. The title compound which is a substituted-1,4-naphthoquinone containing chloro atom and an arylamine with two methoxy group at *m*-position has been recently used for the synthesis of biologically and pharmaceutically important carbazolequinone compounds [19]. The structure of the title compound (Figure 1) was previously elucidated by NMR, IR, and mass spectroscopies and reported [20, 21]. Now, it was confirmed by X-ray diffraction analysis of a single crystal obtained by slow evaporation of an ethyl alcohol solution.

EXPERIMENTAL

Synthesis

Title compound was previously synthesized and prepared by using the following procedure according to the reported literature previously [20, 21]: to a mixture of the 2,3-dichloro-1,4-naphthoquinone (1 g, 4.40 mmol) and 3,5-dimethoxyaniline (0.742 g, 4.84 mmol) in EtOH (100 mL), triethylamine (4.84 mmol, 0.68 mL) was added, and refluxed. The cooled reaction mixture was diluted with dichloromethane and the organic phase was washed twice with water and then

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*Corresponding author. E-mail: niluferbayrak@gmail.com, aftuyun@gmail.com dried over $CaCl_2$. After evaporating the solvent, the crude product was purified by column chromatography on silica gel to yield the 2-(3,5-dimethoxyphenylamino)-3-chloronaphthalene-1,4-dione. Crystals were obtained in good yield.

The solid-state structure of the title compound was confirmed by X-ray diffraction analysis. Data for the title compound was obtained with Bruker APEX II QUAZAR three-circle diffractometer. Indexing was performed using APEX2 [22]. Data integration and reduction were carried out with SAINT [23]. Absorption correction was performed by multi-scan method implemented in SADABS [24]. The Bruker SHELXTL [25] software package was used for structure solution and structure refinement. Aromatic and aliphatic C-bound H atoms were positioned geometrically and refined using a riding mode. Crystallographic data and refinement details of the data collection for the title compound are given in Table 1. Hydrogen-bonding geometry is given in Table 2. The selected bond lengths and bond angles are given in Table 3. Crystal structure validations and geometrical calculations were performed using the Platon software [26]. Mercury software [27] was used for visualization of the .cif files.

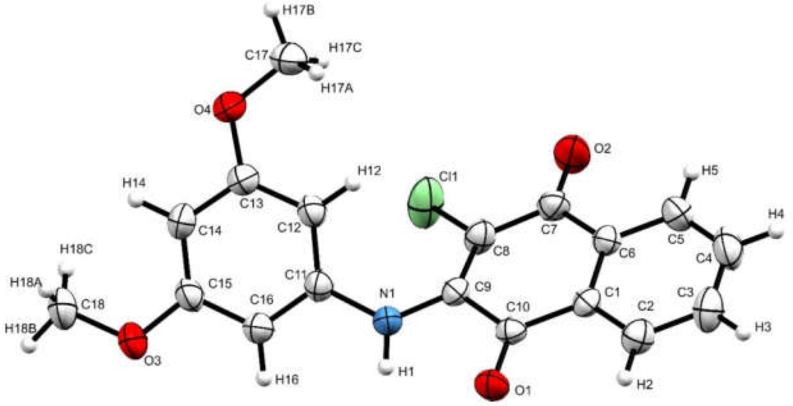

Figure 1. ORTEP drawing of 2-(3,5-dimethoxyphenylamino)-3-chloronaphthalene-1,4-dionedrawn at 50% probability level.

RESULTS AND DISCUSSION

The structural view of the compound with the numbered atoms is depicted in Figure 1. Red plate crystals of 2-(3,5-dimethoxyphenylamino)-3-chloronaphthalene-1,4-dione with the dimensions of 0.076 x 0.152 x 0.428 mm were acquired from the ethanol solution *via* slow evaporation method. The crystal structure is an amino naphthoquinone compound formed from aryl amino and quinoid fragments. These fragments are highly planar and the average deviation of atoms from their rms plane (Δav) is 0.050 $e^-/\text{Å}^3$. However, the whole molecule has a big torsion angles between two cyclic fragments due to nitrogen atom (N1). These torsion angels are -26.6°(5) and -34.8°(5) that correspond to the C12-C11-N1-C9 and C11-N1-C9-C8, respectively. The average carbon-carbon bond lengths in the quinone ring are greater than the carbon-carbon bond lengths in the other ring. In the crystal packing, O1, O2, N1, and Cl1 are involved in hydrogen bonding interactions with the average H···A distance of 2.58 Å and D—H···A angles of 164°. In particular, C5-H5····O1 and N1-H1····O2 atoms make strong hydrogen bonds compared to the others. The detailed geometry of the intermolecular interactions is given in Table 2. As a result, torsion between aryl amino and quinoid planes and the hydrogen bonds form a network (Figure 2). Figure 2 and 3 show stackings formed by the intermolecular interactions.

Table 1. Crystal data, data collection, and structure refinement details for $C_{18}H_{14}ClNO_4$.

Crystal system, space group, Z	Triclinic, P-1, 2
a, b, c α, β, γ	a = 7.0016(6) Å α = 96.037(4)° b = 7.7937(6) Å β = 97.238(4)° c = 15.6218(11) Å γ = 110.388(4)°
V	782.44(11) $Å^3$
d	1.459 g/cm^3
Radiation, λ	MoK α , 0.71073 Å
μ	0.267 mm^{-1}
T	296(2) K
Crystal Size	0.076 x 0.152 x 0.428 mm
F(000)	356
Diffractometer	Bruker AXS
Tmin, Tmax	0.850, 0.980
Theta range, deg	1.33 to 25.00°
Limiting indices	-8<=h<=8, -9<=k<=9, -18<=l<=18
Refinement method	Full-matrix least-squares on F^2
Reflections	Collected 11720, Indepented 2756 [R(int) = 0.0349]
Parameters	219
Final R indices	2297 data; $I>2\sigma(I)$ $R_1 = 0.0525$, $wR_2 = 0.1329$ all data $R_1 = 0.0624$, $wR_2 = 0.1377$
S	1.150
Δρmin /Δρmax	0.247 and -0.357 $eÅ^{-3}$

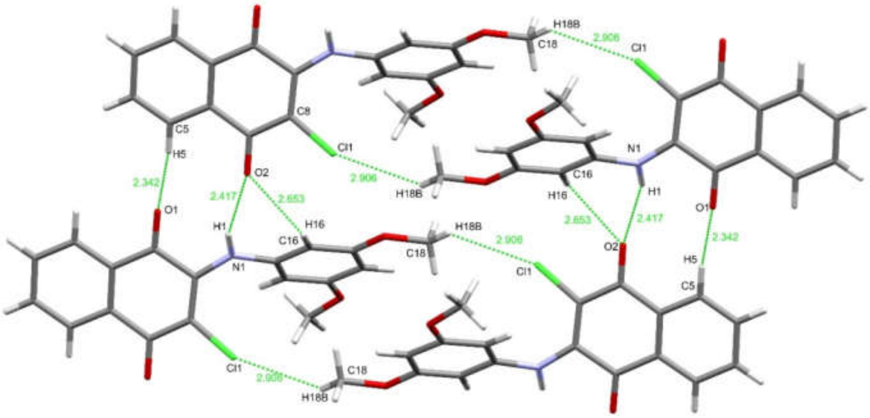

Figure 2. Part of the crystal structure of showing the intermolecular interactions.

Table 2. Hydrogen-bonding geometry (Å).

D—H····A	D—H	H····A	D····A	D—H····A
C5-H5····O1	0.930	2.342	3.247(5)	164.0
N1-H1····O2	0.860	2.417	3.227(3)	157.1
C16-H16····O2	0.930	2.653	3.346(3)	131.9
C18-H18····Cl1	0.961	2.906	3.390(3)	112.3

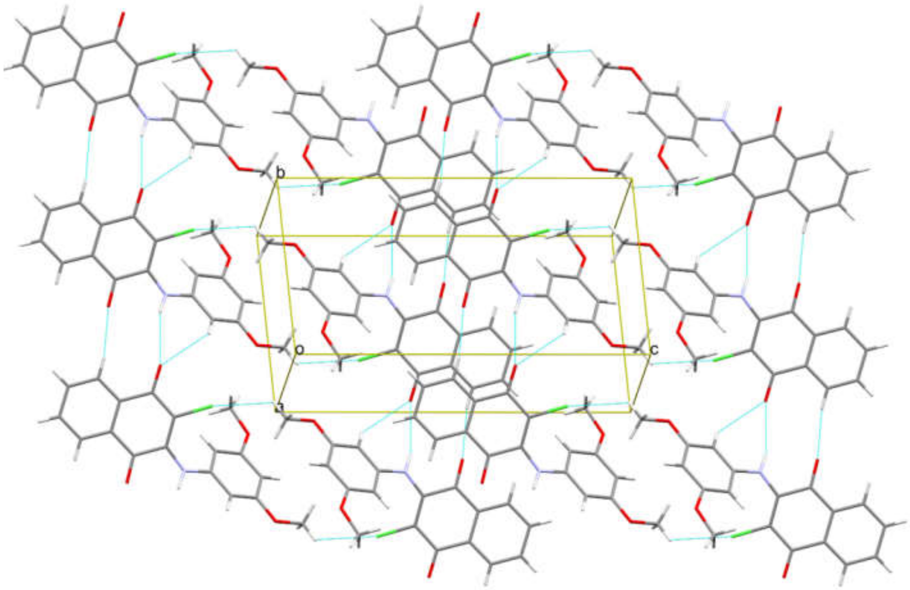

Figure 3. Projection of structure with cell axes, a* view. The hydrogen bonds are shown by dashed lines.

Table 3. Selected bond lengths *d (*Å) and angles ω (˚) in the structure of title compound

Bond	*d*	Angle	ω
C10-O1	1.217(3)	C18-O3-Cl5	117.3(3)
C7-O2	1.224(4)	C13-O4-Cl7	118.9(3)
C15-O3	1.368(4)	C11-N1-C9	128.4(3)
C18-O3	1.416(4)	Cl 1-C8-C9	121.4(3)
C13-O4	1.367(4)	O2-C7-C6	120.7(3)
C17-O4	1.411(4)	O1-C10-C1	122.6(3)
C11-N1	1.412(4)	C12-C11-N1	120.4(3)
N1-H1	0.86	C8-C9-N1	128.9(3)
C9-N1	1.355(4)	C14-C15-O3	123.8(3)
C8-Cl1	1.717(3)	C12-Cl3-O4	123.9(3)

CONCLUSION

The crystal structure revealed that an amino naphthoquinone compound was formed from aryl amino and quinoid fragments. The whole molecule has a big torsion angles between two cyclic fragments due to nitrogen atom (N1). These torsion angels are -26.6°(5) and -34.8°(5) that correspond to the C12-C11-N1-C9 and C11-N1-C9-C8, respectively. The average carbon-carbon bond lengths in the quinone ring are greater than the carbon-carbon bond lengths in the other ring.

SUPPLEMENTARY MATERIAL

The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, and CCDC reference number is 1539522 for the title compound. The data can be obtained available free of charge from http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0)1223336033; email: deposit@ccdc.cam.ac.uk.

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