

X-ray Charge-Density Study of 5-Chloro-8-hydroxy-6-methylnaphthalene-1,4-dione: A Hydroxynaphthoquinone Derivative

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ABSTRACT

The X-ray charge density analysis of a hydroxynaphthoquinone derivative was obtained by multipolar Hansen-Coppens formalism refinement through high resolution X-ray diffraction data at 100(1) K. The molecular properties of the title compound resulted from the combined experimental and the quantum theory of atoms in molecules (QTAIM) studies. The topological properties of the covalent bonds and of the hydrogen bonds have been investigated.

Keywords: X-ray charge density, Hansen-Coppens formalism; QTAIM

INTRODUCTION

Accurate, high-resolution X-ray charge-density experiments provide information on the electron distribution within the system under study, allowing both the nature of the bonding and the atomic interactions to be determined [1]. To this end, Bader's quantum theory of atoms in molecules [2] is a powerful tool, which characterizes the chemical interactions between atoms on the basis of the topological properties of the electron density and the associated Laplacian at bond-critical points (bcps). In organic molecules, envalent bonds are classified as shared shell, while van der Waals (vdW) and hydrogen-bonding interactions are classified as closed-shell.

The electron-density distribution of small molecules, peptides and amino acids carries information which is important in modeling their interactions. The molecular electrostatic potential and electric moments, which may be derived from the charge-density, help to determine the recognition properties such as reactivity in a desired molecule. The electron clouds around atoms in molecules are deformed primarily due to chemical bonding and secondarily by non-bonded interactions such as hydrogen bonds. In the routine crystal structure determination from X-ray diffraction data

using least-squares refinement procedure, the continuous electron-density of molecule is subdivided into independent atomic charge densities, and the basic assumptions are that atoms are neutral and of spherical shape with a radial dependence equal to that of free atoms in the gas phase so-called Independent Atom Model (IAM). So, some corrections due to bonding and non-bonding effects must be considered which leads to multipolar atom model and allows mapping non-spherical electron-density map of the desired molecule.

In this study, the title compound is a substituted 5-hydroxyl-1,4-naphthoquinone (Juglone). Juglone and its 5-acetoxy-2-bromo analogue are the essential dienophile in the highly convergent and regiospecific Diels-Alder synthesis of Ochramycinone, a type of natural anthraquinone which exhibits remarkable antibiotic and antitumor activities. Our aim is to obtain an insight of the nature of the chemical bonds by X-ray charge-density study of the title compound.

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EXPERIMENTAL

The crystal structure of the title compound was determined by single-crystal X-ray crystallography. The crystallographic data of the title compound are listed in Table 1. The ORTEP plot of the title compound based on the IAM refinement was shown in Figure 1, with the 50% probability displacement ellipsoid and atomic numbering. Data were collected on a Bruker SMART APEXII CCD area detector diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) equipped with an Oxford crysystem Cobra low temperature attachment. Cell parameters were retrieved using SMART [5] software and refined using SAINT [6] on all observed reflections. Data reduction and correction for Lp and decay were performed using SAINT Plus software. Absorption corrections were applied using SADABS [7]. The structure was solved by direct methods and refined by the least squares method on F^2 using the SHELXTL program package [8]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined with a riding model approximation with their parameters constrained to the parent atom with $U_{iso}(H) = 1.2$ or $1.5 U_{eq}(C)$, except for the hydrogen atom attached to O3 atom which was located from the difference Fourier map

and constrained to refine with the parent atom with $U_{iso}(H) = 1.5 U_{eq}(O)$.

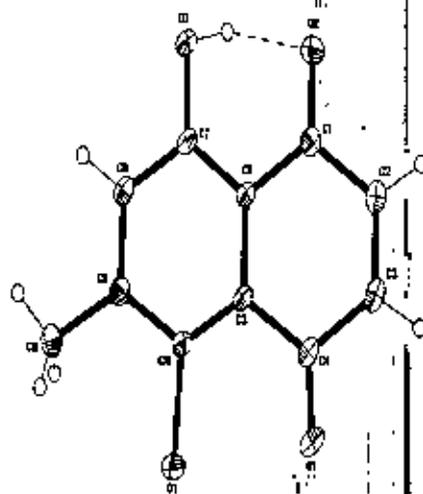


Fig. 1. The ORTEP plot of the title compound based on the IAM refinement with 50% probability displacement ellipsoids and the atomic numbering.

Table 1. The crystallographic data and refinement parameters of the compound by IAM

Empirical formula	C ₁₁ H ₇ ClO ₃
Formula weight	222.62
Temperature	100(1) K
Crystal system	Monoclinic
Space group	C2/c
a(Å)	10.75460(10)
b(Å)	10.31040(10)
c(Å)	16.8370(2)
β (°)	100.2850(10)
V(Å ³)	1836.96(3)
Z	8
D (Mg/m ³)	1.610
μ (mm ⁻¹)	0.395
Crystal size (mm)	0.30 × 0.21 × 0.14
Max. & min. θ	2.76, 35.06
Limiting indices	-12 ≤ h ≤ 17, -16 ≤ k ≤ 16, -27 ≤ l ≤ 27
Reflections collected / unique	17328 / 4015 [R(int) = 0.0309]
Max. and min. transmission	0.9453 and 0.8911
Data / restraints / parameters	4015 / 0 / 140
GoF	1.067
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0380, wR2 = 0.1031
R indices (all data)	R1 = 0.0459, wR2 = 0.1082
Largest diff. peak and hole	0.607 and -0.353 e.Å ⁻³

METHODS

Indeed, accurate low-temperature high resolution X-ray data allow the non-spherical maps, and electron-density to be presented in deformation electron-density maps, and experimentally

quantified by using a non-spherical model of the atomic electron-density and so charge-density is come of age. This model is described as a superposition of pseudo-atoms described by the

multipolar Hansen-Coppens atom formalism (equation 1) [9] in program MoPro [4] which is the most accurate model as follows:

$$\rho_{\text{atom}}(\mathbf{r}) = \rho_{\text{core}}(\mathbf{r}) + P_{\text{val}} \kappa^3 \rho_{\text{val}}(\kappa \mathbf{r}) + \sum_{l=0}^{l_{\text{max}}} \kappa'^3 R_{\text{val}}(\kappa' \mathbf{r}) \sum_{|m| \leq l} P_{lm} Y_{lm}(\theta, \phi) \quad (1)$$

where ρ_{core} and ρ_{val} represent the spherical core and valence unitary electron-density, respectively. P_{val} is the valence population parameter. Y_{lm} represent multipolar spherical harmonic functions of the order l in real form. R_{val} are Slater-type radial functions and P_{lm} are the multipolar populations. The coefficients κ and κ' describe the contraction-expansion for the spherical and multipolar valence densities, respectively. The low X-ray scattering power of H atoms is a well known problem in crystallography. However, as evident from structures based on neutron diffraction experiments (where the scattering length of H atom is comparable in magnitude with those of heavier elements such as carbon and oxygen), the use of an isotropic displacement parameter for hydrogen is a very crude approximation and should be corrected. So, the program SHADE [10] web server was used to model an estimation of hydrogen anisotropic displacement parameters which is based on the analysis of displacement parameters of the non-H frameworks as a rigid body in terms of a TLS (translation-liberation-screw) model by Schomaker and Trueblood method [11]. So, the procedure based on Simple Hydrogen Anisotropic Displacement Estimator (SHADE) calculated the

anisotropic displacement parameters for the hydrogen atoms. A first crystal structure refinement was performed with SHELXTL based on the Independent Atom Model (IAM). Then the least-squares program MoPro was then used to determine the charge-density of the title compound. The anisotropic displacement model of the H-atoms resulted from the SHADE program.

RESULTS AND DISCUSSION

In charge-density results based on multipolar refinement, shared-shell interactions, such as covalent bonds, are characterized by positive values of the electro density and negative values of the Laplacian of the electron density at the bond critical points (bcps), while closed-shell interactions, such as ionic bonding, van der Waals (vdW) and hydrogen bonding, tend to have small positive values for both of the electron density and its Laplacian at the bond critical points (bcps). The topological properties at the critical points identified for the title compound are listed in Table 2. The bond lengths are consistent with aromatic delocalized bonding as anticipated, and four ring critical points (rcps) were identified. Each of the carbon-carbon and carbon-oxygen bonds is a shared-shell covalent interaction. The electron density and Laplacian of C10-C11 bond is also shared-shell but as much as the other covalent bonds which can be substantiated from low values of its electron density ($1.4330 \text{ e.}\text{\AA}^{-3}$) and Laplacian ($-3.80 \text{ e.}\text{\AA}^{-5}$).

Table 2. Topological properties of the title compound at the bond critical points (bcps)

Bond	$R_b(\text{\AA})$	$\rho(r) (\text{e.}\text{\AA}^{-3})$	$\nabla^2 \rho(r) (\text{e.}\text{\AA}^{-5})$
C11-C10	1.7249	1.4330	-3.80
O1-C4	1.2255	2.7972	-15.14
O2-C1	1.2489	2.8145	-24.98
O3-C7	1.3411	2.3074	-21.58
O3-H1O3	0.9392	2.6231	-38.61
C1-C2	1.4621	1.8635	-14.01
C1-C6	1.4658	1.8855	-13.89
C2-H2A	1.0809	1.7766	-15.21
C2-C3	1.3472	2.4332	-22.36
C3-H3A	1.0604	1.8421	-16.61
C3-C4	1.4789	1.9429	-15.41
C4-C5	1.5014	1.8441	-13.38
C5-C6	1.4219	1.9912	-14.00
C5-C10	1.3947	2.1100	-16.63
C6-C7	1.4084	2.1325	-17.78
C7-C8	1.4010	2.1050	-16.10
C8-H8A	1.0358	1.8799	-15.42
C8-C9	1.3842	2.1502	-16.66
C9-C10	1.4202	2.0670	-16.33
C9-C11	1.4977	1.7281	-10.78
C11-H11A	1.0147	1.7433	-12.33
C11-H11B	1.0209	1.7093	-12.81
C11-H11C	1.0256	1.8300	-14.67
C11-O1	2.8197	0.1238	1.83
O2-O3	2.5475	0.2623	5.33

According to the experimental deformation density, polar interactions such as hydrogen bonds have distorting effects on the electron cloud in the region of the oxygen lone pairs. The ORTEP plot of the title compound based on the multipolar refinement formalism with 50% probability displacement ellipsoids and the atomic numbering was shown in figure 2. The multipolar refinement model shows better improvement in the anisotropic displacement parameters of the non-hydrogen atoms with respect to those in the IAM model which can be substantiated from the data presented in Tables 2 and 3, respectively. The $I > 2\sigma(I)$ crystallographic factors are reduced from 0.0380 to 0.0333 for $R(F)$ and from 0.1031 to 0.0397 for $wR(F)$. The anisotropic displacement ellipsoids of the hydrogen atoms (large ellipsoids in figure 2) were calculated by SHADE program. The deformation density map, Laplacian of the electron density, electrostatic potential map, and the gradient paths of the title compound were shown in Fig. 3, 4, 5, and 6, respectively.

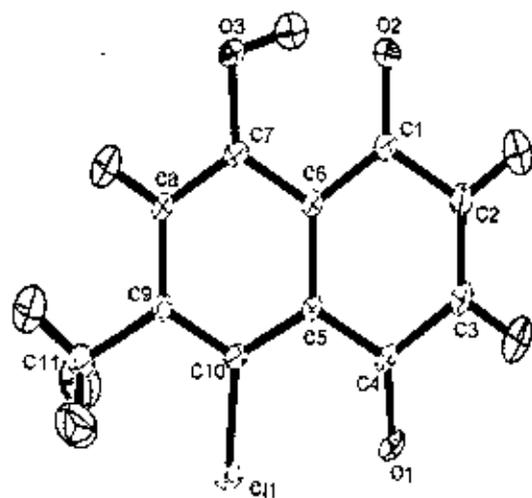


Fig. 2. The ORTEP plot of the title compound based on the multipolar refinement with 50% probability displacement ellipsoids and the atomic numbering. The anisotropic displacement ellipsoids of the hydrogen atoms were calculated by SHADE program.

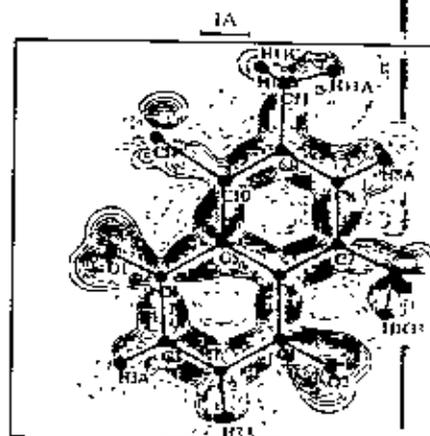


Fig. 3. Experimental deformation density maps in the plane of the title compound (contours at 0.1 e^{-3} , blue/red: positive/negative).

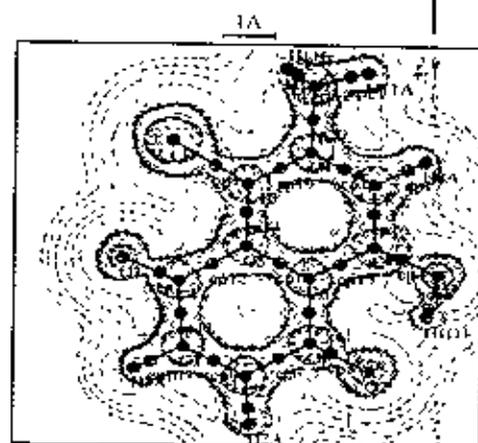


Fig. 4. Laplacian of the electron density for the title compound, positive contours are dashed red lines, while negative contours are dashed blue lines.

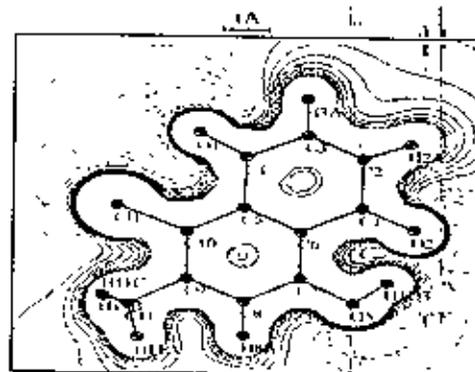


Fig. 5. Electrostatic potential generated around the molecule (Contours, 0.1 e^{-4} , continuous blue line positive and dashed red line, negative).

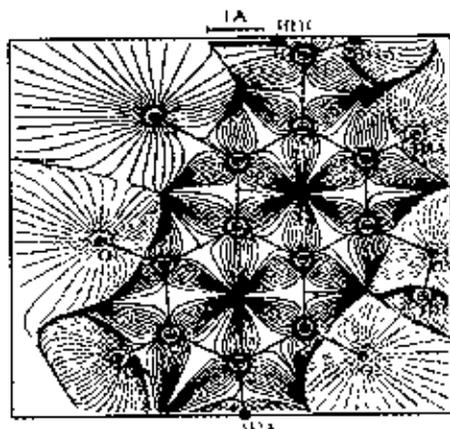


Fig. 6. Representation of the gradient lines of the total electron density in the plane of the title molecule.

CONCLUSION

The experimental charge-density analysis for the title compound at 100(1) K afforded a good multi-polar refinement and improvement of the crystallographic $R(F)$ and $wR(F)$ factors with respect to the IAM refinement. The resulted shared- and closed-shell interactions are in good agreement with the model as presented in Table 2.

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