



THE CRYSTAL STRUCTURE OF $\text{Os}_3(\text{CO})_{11}(\text{PPh}_2(\text{C}_{10}\text{H}_7))\cdot\text{H}_2\text{O}$: A COMBINED HIRSHFELD SURFACE ANALYSIS AND DFT CALCULATIONS

(Struktur Hablur $\text{Os}_3(\text{CO})_{11}(\text{PPh}_2(\text{C}_{10}\text{H}_7))\cdot\text{H}_2\text{O}$: Gabungan Analisis Permukaan Hirshfeld dan Pengiraan DFT)

Husna Izzati Muhammad Nor Azharan¹, Enis Nadia Md Yusof², Suhana Arshad³,
Omar Bin Shawkataly⁴, and Siti Syaida Sirat^{1,5*}

¹Faculty of Applied Sciences, Universiti Teknologi MARA, Cawangan Negeri Sembilan, Kampus Kuala Pilah,
72000 Kuala Pilah, Negeri Sembilan, Malaysia

²Chemistry Section, School of Distance Education, Universiti Sains Malaysia, 11800, Minden, Penang, Malaysia

³X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, USM, Penang, 11800, Malaysia

⁴Academy of Sciences Malaysia, Level 20, West Wing, MATRADE Tower, Jalan Sultan Haji Ahmad Shah,
off Jalan Tuanku Abdul Halim, 50480 Kuala Lumpur, Malaysia

⁵Atta-ur-Rahman Institute for Natural Product Discovery (AuRIns), Universiti Teknologi MARA, Kampus Puncak Alam,
42300 Bandar Puncak Alam, Selangor, Malaysia

*Corresponding author: sitisyaida@uitm.edu.my

Received: 25 January 2023; Accepted: 8 May 2023; Published: 23 June 2023

Abstract

The molecular structure of $\text{Os}_3(\text{CO})_{11}(\text{PPh}_2(\text{C}_{10}\text{H}_7))\cdot\text{H}_2\text{O}$ was investigated by a single crystal X-ray diffraction. The compound crystallizes in the triclinic, *P*-1 space group with unit cell parameters $a = 12.4377(14)$, $b = 12.4413(13)$, $c = 12.4718(13)$ Å, $\alpha = 87.3030(19)$, $\beta = 63.7889(17)$ and $\gamma = 79.3982(19)^\circ$. The asymmetric unit of this structure consists of one-triangulo-triosmium complex molecule and one water molecules. The crystal packing of the title compound is stabilized by $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds as well as $\text{C}-\text{H}\cdots\pi$ interaction. The intermolecular interactions were investigated by Hirshfeld surfaces analysis, showing high contribution of $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ contacts. The molecular electrostatic potential and frontier molecular orbitals of the title compound were further investigated using Density Functional Theory (DFT), revealing that the nucleophilic regions are located at the carbonyl group. There is a large energy gap (6.095 eV) between HOMO and LUMO.

Keywords: triosmium, phosphine ligand, Hirschfeld surface analysis, crystal structure

Abstrak

Struktur molekul $\text{Os}_3(\text{CO})_{11}(\text{PPh}_2(\text{C}_{10}\text{H}_7))\cdot\text{H}_2\text{O}$ telah disiasat melalui pembelauan sinar-X hablur tunggal. Sebatian itu menghablur dalam kumpulan ruang triklinik, *P*-1 dengan parameter sel unit $a = 12.4377(14)$, $b = 12.4413(13)$, $c = 12.4718(13)$ Å, $\alpha = 87.3030(19)$, $\beta = 63.7889(17)$ dan $\gamma = 79.3982(19)^\circ$. Unit asimetri struktur ini terdiri daripada satu molekul kompleks *triangulo-triosmium* dan satu molekul air. Pembungkusan hablur sebatian distabilkan oleh ikatan hidrogen $\text{O}-\text{H}\cdots\text{O}$ dan $\text{C}-\text{H}\cdots\text{O}$ serta interaksi $\text{C}-\text{H}\cdots\pi$. Interaksi antara molekul telah disiasat oleh analisis permukaan Hirshfeld, menunjukkan $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ adalah penyumbang utama interaksi. Potensi elektrostatis molekul dan orbital molekul sempadan bagi sebatian ini telah disiasat

selanjutnya menggunakan Teori Fungsian Ketumpatan (DFT), mendedahkan bahawa kawasan nukleofilik terletak pada kumpulan karbonil. Terdapat jurang tenaga yang besar (6.095 eV) antara HOMO dan LUMO.

Kata kunci: triosmium, ligan fosfina, analisis permukaan Hirshfeld, struktur hablur

Introduction

The chemistry of triosmium metal clusters with simple substituted tertiary phosphine has been thoroughly studied [1, 2, 3]. Several triosmium metal clusters were reported to exhibit a wide range of catalytic activity [4]. The geometric structure of the metal clusters significantly impact important catalytic activity in which certain geometric structures may interact with the intermediates in the catalytic process. Besides, metal clusters may give an insight to reaction mechanism that have limitations in mononuclear chemistry [5]. Due to their potential application in the catalysis, exploring new triosmium cluster with monodentate phosphine ligands is our research interest. In this study, the $\text{PPh}_2(\text{C}_{10}\text{H}_7)$ (diphenylphosphinonaphthalene) ligand has been selected for substitution with $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ due to its versatility as a chiral ligand in some catalytic reaction [6, 7]. The reaction produced $\text{Os}_3(\text{CO})_{11}(\text{PPh}_2(\text{C}_{10}\text{H}_7))\cdot\text{H}_2\text{O}$ (**1**) in moderate yield and was successfully determined by a single-crystal X-ray diffraction. The crystal structure of this triosmium cluster was previously obtained from the reaction between $\text{Os}_3(\text{CO})_{12}$ and 1,8-bis(diphenylphosphino)naphthalene (dppn) in the presence of trimethylamine oxide [8]. However, the previously reported crystal structure is slightly different from the title compound. The reported structure contains a dichloromethane whereas the title compound contains a water molecule. The title compound was synthesized using a different synthesis method. The present paper describes the X-ray crystallographic structure analysis, Hirshfeld surface analysis, and Density Functional Theory (DFT) calculations.

Materials and Methods

General techniques

All synthesis work was carried out under an oxygen-free-nitrogen (OFN) atmosphere using standard Schlenk techniques. Chemicals were purchased from Sigma-Aldrich and used as received. $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ and (diphenylphosphinonaphthalene) ($\text{PPh}_2(\text{C}_{10}\text{H}_7)$) were prepared by the published procedure [6, 9]. The IR

spectrum was recorded with a solid sample on an Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR), Perkin Elmer 2000 FT-IR spectrometer. NMR spectra were recorded using a Bruker Ascend 500 MHz Spectrometer operating at 500 MHz (^1H) and at 202 MHz (^{31}P). Chemical shifts are given in ppm relative to TMS (^1H) and 85% H_3PO_4 (^{31}P). Product separation was performed on glass plates (20 X 20 cm) coated with 0.5 mm Silica Gel (Merck, 60GF₂₅₄).

Synthesis and crystallization of **1**

A solution of $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ (80 mg, 0.087 mmol) and $\text{PPh}_2(\text{C}_{10}\text{H}_7)$ (26 mg, 0.087 mmol) in dichloromethane (CH_2Cl_2) (25 mL) was stirred at room temperature for 60 min. The solution was dried *in-vacuo* and the residue chromatographed by preparative thin layer chromatography on silica gel with $\text{C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ (3:2) as the eluent. The desired product was isolated as the second (yellow) band in 50% yield and recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$. IR (ATR): $\nu(\text{CO})$ 2105m, 2050sh, 2011s, 2001s, 1984s, 1950s cm^{-1} . ^1H NMR (CDCl_3): δ 7.98-7.41 (m, 17H, Ph, C_{10}H_7). ^{31}P NMR (CDCl_3): δ -2.34 ppm ($\text{PPh}_2(\text{C}_{10}\text{H}_7)$).

Single crystal X-ray diffraction

The single crystal X-ray diffraction study were grown from solvent-solvent diffusion of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ and collected on a Bruker SMART APEXII-DUO CCD area-detector diffractometer with graphite monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The collected three-dimensional intensity data was performed using the APEX2 software [10], where the cell refinement and data reduction were performed using the SAINT program [10]. The structure was solved by direct method using the program SHELXLTL [11] and refined by full-matrix least-squares technique on F^2 . The absorption correction was applied to the final crystal data using the SADABS software [10]. All the geometrical calculations were carried out using the program PLATON [12]. The anisotropic displacement parameters were refined for all non-hydrogen atoms. The molecular graphic and packing diagrams were drawn using

Mercury program [13].

Density functional theory (DFT) calculation

All DFT calculations were performed using the Gaussian09 [14] and the Gaussview5 software [15]. The initial molecular structure and geometry of **1** was obtained from the X-ray crystallographic data. The optimization of the geometry structure was achieved using M06-2X exchange correlation functional [16, 17] with LanL2DZ pseudopotential on Os and 6-31(d, p) Pople basis set for all other atoms [18, 19, 20]. The harmonic frequency calculations were performed at the same level of theory and the stationary points were verified to have no imaginary frequencies.

Results and Discussion

Single crystal X-ray diffraction

The molecular structure of the title compound consists a triangular arrangement of three Os atoms. The $\text{PPh}_2(\text{C}_{10}\text{H}_7)$ occupies the equatorial site with an assigned numbering scheme, as can be seen from Figure 1(a). Figure 1(b) is an optimize structure obtained by Density Functional Theory (DFT) calculation. The crystal structure of **1** is crystallized in a triclinic *P*-1 space group and successfully refined with unit cell parameters, $a = 12.4377(14)$ Å, $b = 12.4413(13)$ Å, $c = 12.4718(13)$ Å, $\alpha = 87.3030(19)^\circ$, $\beta = 63.7889(17)^\circ$, $\gamma = 79.3982(19)^\circ$ and $Z = 2$. The crystal data and refinement

details are presented in Table 1. The crystal of **1** differs to the previously reported structure by virtue of containing a water solvate. Selected bond length and bond angles are listed in Table 2. The bond length and bond angles from the X-ray diffraction are comparable to DFT calculation. The longest Os–Os bond (Os1–Os3) in **1** is Os–Os *cis* to $\text{PPh}_2(\text{C}_{10}\text{H}_7)$. This has been observed in many other $\text{Os}_3(\text{CO})_9(\text{PR}_3)$ [where $\text{PR}_3 = \text{Group 15 monodentate ligand}$]. The elongation of this bond length has been ascribed to the effect of substituting a CO ligand with a PR_3 ligand [1, 21]. PR_3 ligand is a good σ -donor that promotes a higher electron density in the Os framework which is relieved by expansion [21]. The $\text{PPh}_2(\text{C}_{10}\text{H}_7)$ occupy equatorial position on Os1 with the value of Os–P bond length is 2.378 (2) Å and comparable to those in $\text{Os}_3(\text{CO})_{11}\text{PPh}_3$ [2.370(2) Å] [1], $\text{Os}_3(\text{CO})_{11}\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3$ [2.374(3) Å] [2], $\text{Os}_3(\text{CO})_{11}(\eta^1\text{-}^i\text{Bu}_2\text{PC}_2\text{H}_4\text{CN})$ [2.394(5) Å] [6]. The Os–C(CO) bond lengths are in the range 1.880(8) - 1.963(10) Å, average 1.933 Å and in a good agreement with expected values [1, 2]. The Os–C–O bond angles (at equatorial) are essentially linear in the range from 176.97–179.65° whereas the Os–C–O bond angles (at axial) are 174.68–176.01°. In the crystal packing, the molecular structure of **1** is linked by O–H $\cdots$ O and C–H $\cdots$ O hydrogen bonds as shown in Figure 2. The presence of C–H $\cdots$ π interactions (Table 3) further stabilized the crystal structure.

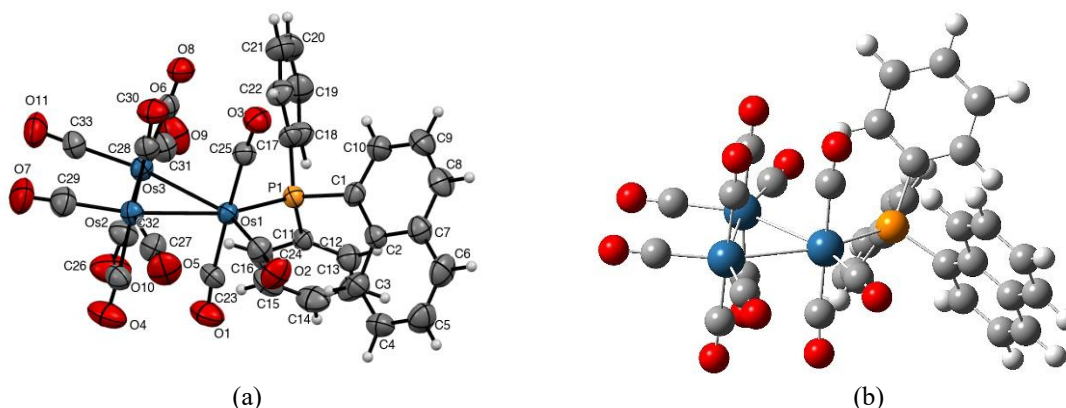


Figure 1. (a) Molecular structure of **1** by X-ray diffraction and (b) the optimized structure performed in DFT at M06-2X/LanL2DZ/6-31(d,p) level of theory. (H_2O molecule is omitted for clarity)

Table 1. Crystal data of **1**

CCDC No	2219979
Chemical formula	$\text{C}_{33}\text{H}_{19}\text{O}_{12}\text{Os}_3\text{P}$
Formula weight	1209.05
T(K)	297(2)
λ (Å)	0.71073
Crystal system	triclinic
Space group	<i>P</i> -1
Unit cell dimensions	
<i>a</i> (Å)	12.4377(14)
<i>b</i> (Å)	12.4413(13)
<i>c</i> (Å)	12.4718(13)
α (°)	87.3030(19)
β (°)	63.7889(17)
γ (°)	79.3982(19)
<i>V</i> (Å ³)	1700.6(3)
<i>Z</i>	2
Density (calculated) (g/cm ³)	2.361
<i>F</i> (0 0 0)	1112
Absorption coefficient (mm ⁻¹)	11.289
Crystal size (mm)	0.10 x 0.24 x 0.39
θ Range (°)	1.9-35
Reflections collected/unique	23334/8876
<i>R</i> _{int}	0.049
Data/restraints/parameter	8876/0/442
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.0477, 0.1464, 1.02
Largest difference in peak and hole (e Å ⁻³)	4.00 and -2.48

Table 2. Selected bond lengths and bond angles of **1**

Bond	Bond Length (Å) (X-ray Diffraction)	Bond Length (Å) M06-2X/LanL2DZ/6-31(d,p)
Os1–Os2	2.8881 (5)	2.86587
Os1–Os3	2.9077(5)	2.91398
Os2–Os3	2.8838 (4)	2.89236
Os1–P1	2.378 (2)	2.37501
Os1–C23 _{ax}	1.950 (8)	1.94612
Os1–C24 _{eq}	1.880 (8)	1.88889
Os1–C25 _{ax}	1.930 (8)	1.94024
Os2–C26 _{ax}	1.948 (10)	1.95390
Os2–C27 _{eq}	1.932 (9)	1.91539
Os2–C28 _{ax}	1.956 (9)	1.95452
Os2–C29 _{eq}	1.903 (10)	1.91407
Os3–C30 _{ax}	1.963 (10)	1.94649
Os3–C31 _{eq}	1.917 (9)	1.91198
Os3–C32 _{ax}	1.958 (10)	1.94641
Os3–C33 _{eq}	1.924 (9)	1.91676

P1–C1	1.841 (7)	1.84103
O10–C32	1.131 (12)	1.14625
O11–C33	1.113 (11)	1.14550
Bond	Bond Angle (°) (X-ray Diffraction)	Bond Angle (°) M06-2X/LanL2DZ/6-31(d,p)
Os2–Os1–Os3	59.677(10)	60.049
P1–Os1–Os3	103.11(5)	100.466
P1–Os1–Os2	162.52(5)	160.514
Os1–C23 _{ax} –O1	173.6(9)	174.678
Os1–C24 _{eq} –O2	174.8(8)	176.972
Os1–C25 _{ax} –O3	174.8(7)	175.161
Os2–C26 _{ax} –O4	173.2(9)	175.906
Os2–C27 _{eq} –O5	177.6(10)	179.502
Os2–C28 _{ax} –O6	174.9(8)	176.009
Os2–C29 _{eq} –O7	178.6(10)	179.604
Os3–C30 _{ax} –O8	175.4(7)	175.830
Os3–C31 _{eq} –O9	176.6(9)	178.289
Os3–C32 _{ax} –O10	174.1(9)	175.737
Os3–C33 _{eq} –O11	178.3(9)	179.653

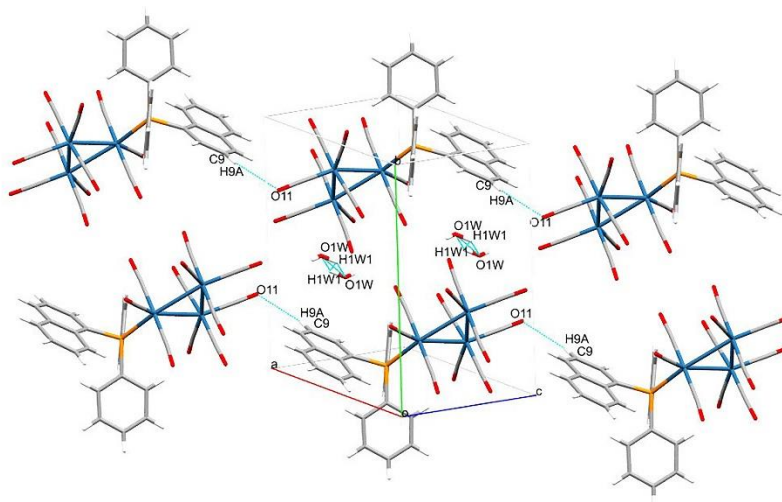


Figure 2. Packing diagram of **1** showing O–H···O and C–H···O interactions

Table 3. Hydrogen bond geometries of **1** (Å, °)

D–H···A	D–H	H···A	D···A	D–H···A	Symmetry Code
O1W–H1W1···O1W ⁱ	0.85	2.28	2.837 (17)	124	(i) 1-x,-1-y,-z
C9–H9A···O11 ⁱⁱ	0.93	2.60	3.370 (14)	141	(ii) -1+x, y, 1+z.
C18–H18A···Cg3 ⁱ	2.86	143	3.649 (12)	22	(i) x,y,z
C19–H19A···Cg1 ⁱⁱ	2.83	132	3.528 (12)	62	(ii) 1-x,-y,-z
C19–H19A···Cg5 ⁱⁱ	2.78	143	3.568 (12)	63	(ii) 1-x,-y,-z

Cg3, Cg1, Cg5 are the centroid of C11–C16, C1–C2–C7–C8–C9–C10, C1–C10, respectively.

Frontier molecular orbitals

The highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) are called as frontier molecular orbitals which principally determine the kinetic stability and reactivity of molecules [22]. The HOMO orbitals are mainly located at triangular Os atoms, CO groups and partially on the two phenyl rings. In contrast, the distribution of the

LUMO orbitals are prominently accumulated at the naphthalene ring. The distribution of HOMO and LUMO are shown in Figure 3. The HOMO and LUMO orbitals are lying at -6.974 eV and -0.879 eV, respectively. Therefore, the energy gap is 6.095 eV. Generally, a larger energy gap implies a high kinetic stability and low chemical reactivity [23,24].

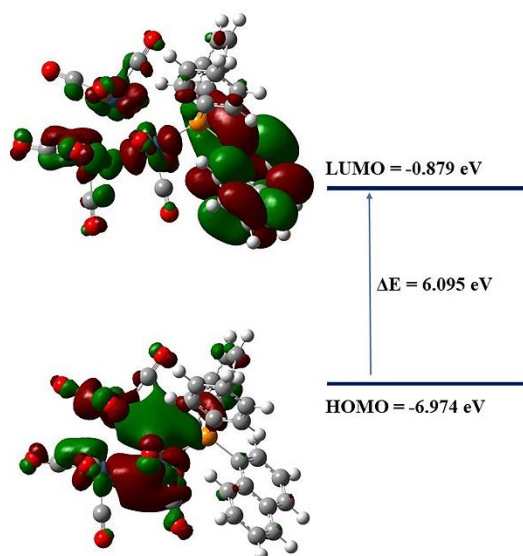


Figure 3. The HOMO-LUMO diagram of **1**

Molecular electrostatic potential

The molecular electrostatic potential (MEP) surfaces are regions around the molecule that provides a relevant guide about the net electrostatic effect at a point by the total charge distribution around the molecule. It also correlates with dipole moments, electronegativity, partial charges, and chemical reactivity of the molecule [25]. The MEP surface is computed using DFT at the 0.0004 a.u. isodensity surface, illustrated in Figure 4. As shown in the surface of **1**, the color code of the map gives the range values between -3.025×10^{-2} a.u (red)

towards -3.025×10^{-2} a.u (blue). The regions of the respective colors indicating the most negative electrostatic potential (red) and the most positive electrostatic potential (blue) while zero electrostatic potential (green). The MEP surface showed the most negative regions (red) around the carbonyl groups which can be considered as possible nucleophilic sites. In contrast, the blue region indicates the positive regions suggesting electrophilic sites which are observed at the phenyl and naphthalene ring.

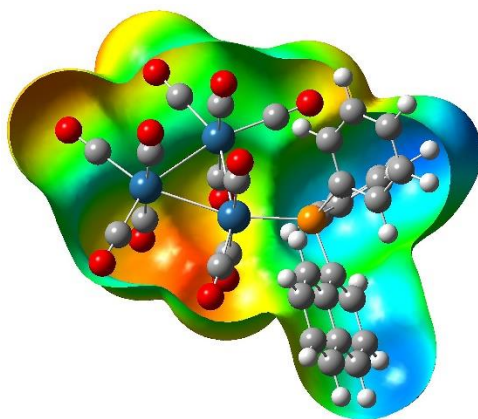


Figure 4. Molecular electrostatic potential diagram of **1**

Hirshfeld surface analysis

Hirshfeld surfaces and the associated 2D fingerprint were calculated using the CrystalExplorer 17.5 [26]. The Hirshfeld surface analysis was used to validate the contributions of the various intermolecular interactions in the crystal structure [27]. The 3D d_{norm} surface of the title compound is shown in Figure 5. The bright-red spot on the d_{norm} surface indicating the presence of strong hydrogen bond which connects the adjacent molecules via O1W–H1W1...O1W interaction. The 2D fingerprint plots of a Hirshfeld surfaces were successfully elucidated and delineated into O...H/H...O, H...H, C...H/H...C, O...O, O...C/C...O and C...C contacts are shown in Figure 6. The most dominant contributor on the Hirshfeld surface corresponding to the O...H/H...O contacts with the percentage of 42.8% correspond to C–H...O and O–H...O interactions. H...H (17.6%) contacts

are the second largest contributor out of the overall Hirshfeld surface. The C...H/H...C (15.4%) contacts represented by the two wings of spike in the region ($d_e \sim 1.6$ Å, $d_i \sim 1.0$ Å). The other contacts which are O...O, and O...C/C...O, show the percentage contributions of 11.6% and 11.2%, respectively. The fingerprint of O...C/C...O shows a pair of spikes at ($d_e \sim 1.7$ Å, $d_i \sim 1.5$ Å). The least significant contributions come from the C...C contacts (1.3%) with respect to the total Hirshfeld surface area. On the other hand, the participation of C–H... π interactions can be further visualized under the shape-index surface mapping as illustrated in Figure 7. The presence of the orange spot indicates the existence of C–H... π interactions in the aromatic rings. These intermolecular interactions help to further stabilize the crystal structure of **1** [28].

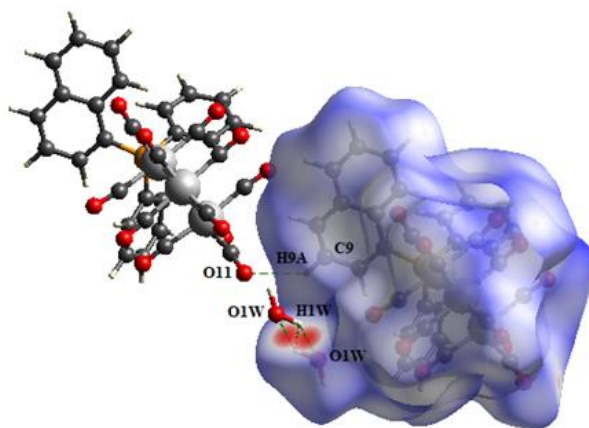


Figure 5. The 3D d_{norm} surface of **1**

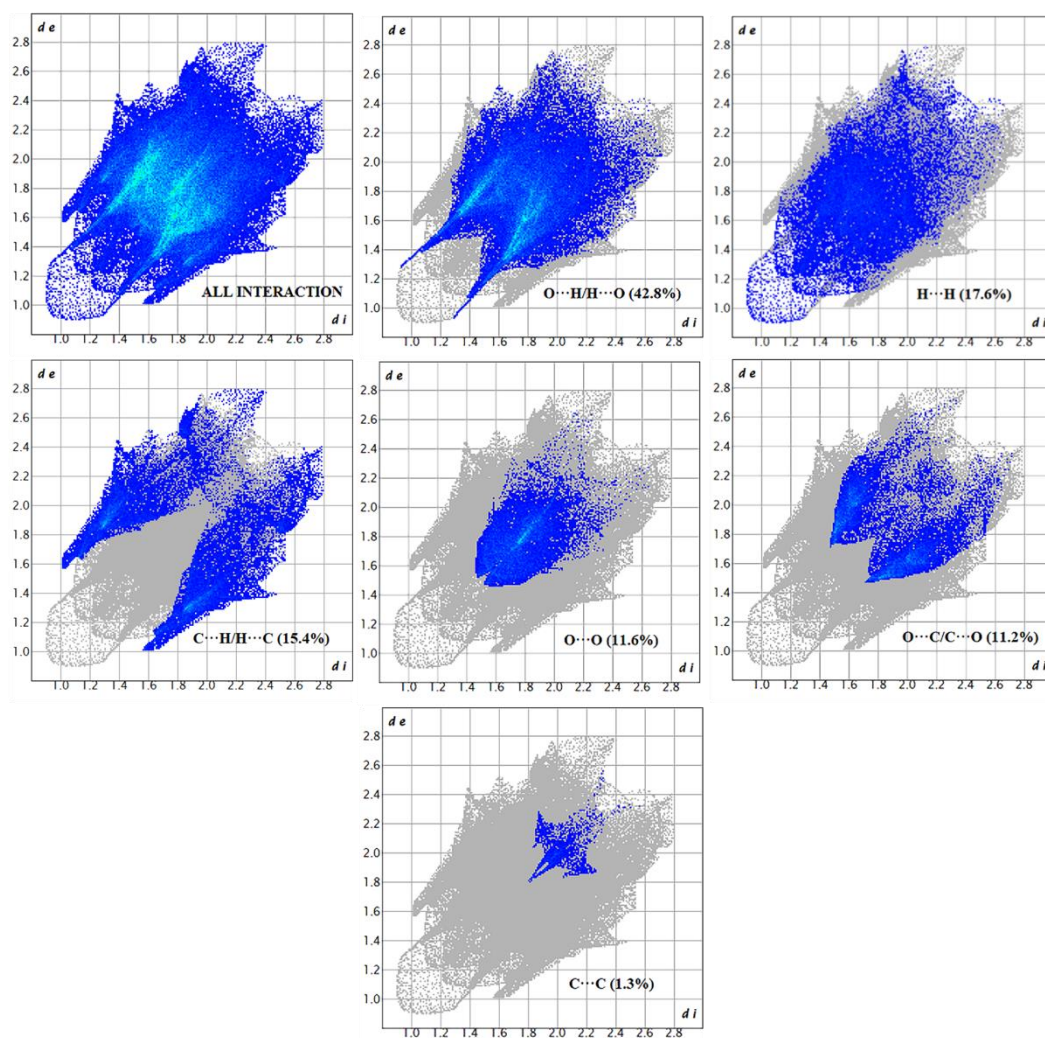


Figure 6. The 2D fingerprint plots of **1** with their respective percentage contribution

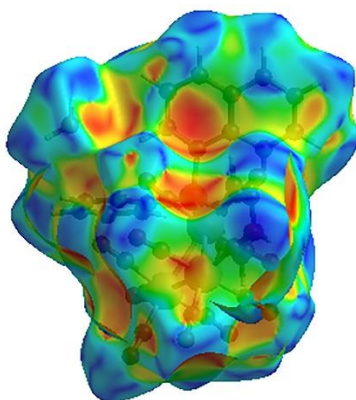


Figure 7. Surface property mapped under shape index of **1**

Conclusion

A new structure of **1** was synthesized and confirmed by spectroscopy characterization and single crystal X-ray diffraction. The molecular structure optimized by DFT is consistent with the crystal X-ray diffraction data. Based on the comparison between the geometry parameters such as bond distances and bond angles, the values of the X-ray diffraction data fall within the expected range of the theoretical data by DFT. The Hirshfeld surface analysis reveal that the intermolecular interactions are dominated by O...H/H...O contacts with 42.8% contribution of total Hirshfeld surfaces, which stabilize the crystalline structure. In addition, the analysis on the frontier molecular orbital showed the title compound possess large energy gap (6.095 eV) which could be attributed to high kinetic stability.

Supplementary material

CCDC-2219979 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/consts/retrieving.html (or from the Cambridge Crystallographic data centre (CCDC), 12, Union Road, Cambridge CB2 1E2, UK, Fax: C44 (0)1223- 336033; email-deposit@ccdc.cam.ac.uk).

Acknowledgement

The authors are grateful to Dr. Imthyaz Ahmed Khan for the guidance in the synthesis of the title compound. SSS acknowledged Ministry of Higher Education, Malaysia under the Fundamental Research Grant Scheme (FRGS) (Project Number: FRGS/1/2021/STG04/UITM/02/4) for financial support.

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