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Jamil Khan*, Bakhtiar Muhammad, Shabnam Shahida, Khizar Hussain Shah, Muhammad Imran Irfan, Tauqeer Ahmad, Muhammad Fahad

2-formyl-3,6-bis(hydroxymethyl)phenyl benzoate in Electrochemical Dry Cell

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Abstract: Solvated organic compound with the general formula 2-formyl-3,6-bis(hydroxymethyl)phenyl benzoate [$C_{16}H_{14}O_5$] was synthesized. Fourier-transform infrared (FTIR), Mass Spectrometry (MS) and X-ray powder analytical methods were used here for structure elucidation. Characterization revealed a triclinic geometry with space group P1. The refined unit cell parameters are, a = 15.196 Å, b = 14.882 Å and c = 14.606 Å. Development in present work is an idea of the organic electrochemical dry cell. Electrochemists with an idea in *vitro/vivo* development in present assay are openly encouraged for supporting exploration.

Keywords: synthesis; crystal structure; electrochemical dry cell.

1 Introduction

Electrochemical dry cell is an autonomous plant that produces energy like normal electricity. Indeed, usually released over a period of a minute, hours, days or even years wherever it's required [1]. In the 20th century, electrochemical dry cells have been documented as the most common power sources used for portable electronic devices such as cameras, phones, computers, cars and clocks etc. Normally, a typical cell is composed of two different electrodes separated by an insulator, a slightly porous rod cathode and metal cylinder serves as both a container and the anode. The space between the cathode and anode is taken up by electrolyte in the form of a paste. Dry cells work through the cell's reaction and generate electrons on the anode. This causes a potential difference between cathode and anode. The paste retains these electrons and will be able to get rid when conductive path is hooked up to the cell [2]. Finally, the cell was sealed with a layer that conducts a potential as shown in the Figure 1.

Once the cell is connected to the DC power supply inside the circuit, two processes take place which are called discharging and charging. The cell started charging when the DC power supply was plugged in from the circuit. The voltage difference is created within circuit. Once the potential at the terminals of the cell was equal to the applied voltage of power supply, the charging phase was completed. The cell began to discharge when the DC power supply of the circuit is switched off [3]. Dry cell is now commercially available and most of the cell currently available are based on activated carbon electrodes and an

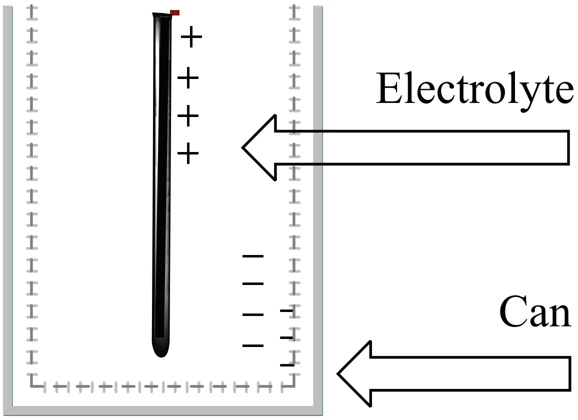
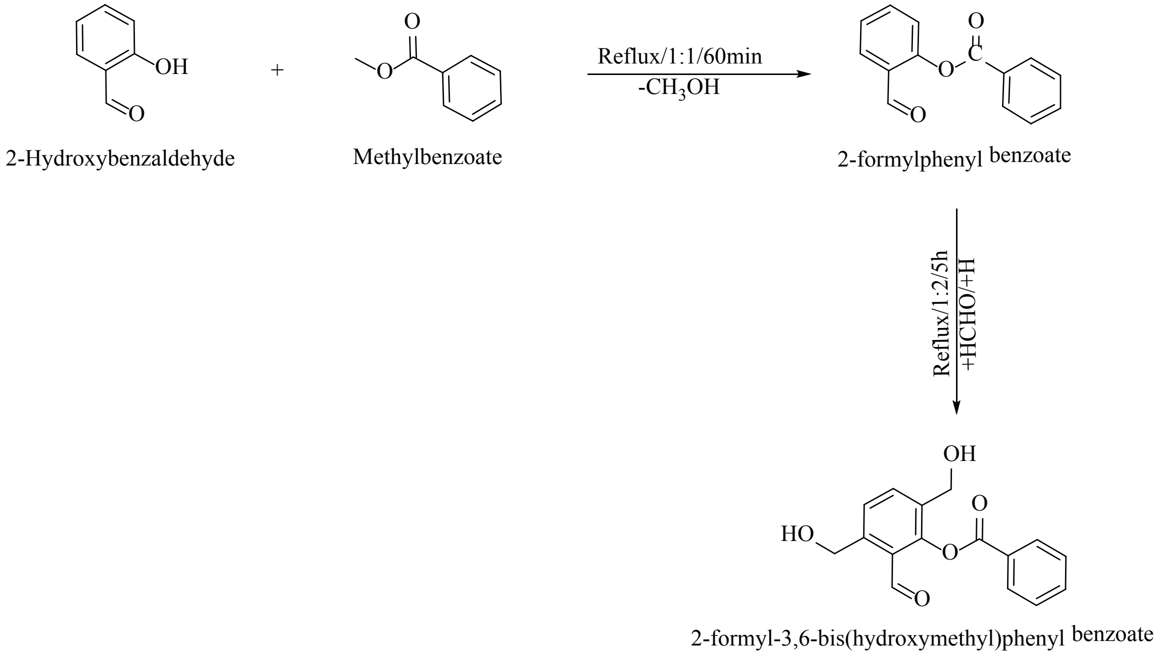


Figure 1: Electrochemical dry cell.

***Corresponding author: Jamil Khan,** Department of Chemistry, Hazara University Mansehra, Pakistan; Department of Chemistry, COMSATS University Islamabad, Abbottabad Campus, Pakistan, E-mail: jamilkhan@ciit.net.pk
Bakhtiar Muhammad: Department of Chemistry, Hazara University Mansehra, Pakistan
Khizar Hussain Shah, Muhammad Fahad: Department of Chemistry/Electrical Engineering, COMSATS University Islamabad, Abbottabad Campus, Pakistan
Shabnam Shahida: Department of Chemistry, University of Poonch, Rawalakot Azad Jammu and Kashmir, Pakistan
Muhammad Imran Irfan: Department of Chemistry, University of Sargodha, Sargodha, Pakistan
Tauqeer Ahmad: Department of Chemistry, University of Sargodha, Sub-Campus Mainwali, Pakistan



Scheme 1: Synthesis of 2-formyl-3,6-bis(hydroxymethyl)phenyl benzoate.

organic electrolyte. The organic electrolytes are preferred by industry to aqueous ones due to of their high stability window. However, the performance and the cost of the cell are the main parameters. This requires fundamental understanding and correct principles of action. For these reasons, various strategies have been proposed in the literature, which include the development of new electrodes, electrolytes and geometries [4].

2 Experimental

Analytical grade solvents and metal salts, etc. were purchased from Fluka Chemicals and used without further purification. Glassware was carefully washed and all the reactions were carried out under a nitrogen atmosphere. IR spectrum was recorded on a FTIR-165 Bio-Rad Marlin Spectrophotometer. Mass spectrum was determined on a Clarus 600MS of Perkin Elmer, USA. The XRD diffraction pattern was measured continuously by Oxford Gemini Ultra R. The electrochemical measurements were carried out at Electrical Power Laboratory, COMSATS University Islamabad, Abbottabad Campus, Pakistan.

2.1 Synthesis of 2-formyl-3,6-bis(hydroxymethyl)phenyl benzoate

The reaction steps involved in the synthesis of titled compound is shown in Scheme 1. The 2-formyl-3,6-bis(hydroxymethyl)phenyl benzoate was prepared according to the literature method from 2-hydroxybenzaldehyde and methyl benzoate in 50ml formaldehyde solution in a 1:1 ratio [5]. This reaction was refluxed with continuous stirring equipped with a Dean Stark apparatus for 5 h at 313 K until TLC indicated that the reaction was complete. The solvent was filtered, evaporated and concentrated under vacuum. The concentrate was rinsed with brine (100 mL) and the remaining was eluted from a column of silica gel to give 70% yield as a brown solid. Compound was recrystallized from a formaldehyde solution containing 10-15% methanol as stabilizer, 37 wt. % in water. IR (cm^{-1}; KBr pellet): υ (OH) = 3457, υ (CH) = 2830, υ (CO) = 1735, υ (CH) = 3000, υ (CO) = 1192, υ (CC) = 1535. MS (EI, 70 eV): m/z (%) 284-2H (10) [M^+], 207 (90), 163 (18), 133 (32), 103 (22), 71 (35), 43 (44), 29 (33). PXRD reflections °2Th. (%): 5.97 (100.00), 6.06 (73.22), 8.35 (36.28), 11.91 (9.31), 13.18 (8.14), 19.38 (1.29).

Table 1: X-ray crystallographic data for 2-formyl-3,6-bis(hydroxymethyl)phenyl benzoate.

Chemical formula	$C_{16}H_{14}O_5$
M_r	286.27
Crystal system, space group	Triclinic, P1
A	15.196 Å
B	14.882 Å
C	14.606 Å
α	88.14 °
β	92.26 °
γ	87.48 °
V	3295 Å^3
Z	1
F(000)	150
Dx	0.144 Mg m^{-3}
Mo Kα radiation, λ	1.540562, 1.544390 Å
Particle morphology	Plate-like white flat sheet 25 × 25 mm
Specimen preparation	Prepared at 438 K
Data collection	Oxford Gemini Ultra R diffractometer
Monochromator	Graphite
Detector resolution	10.3457 pixels mm^{-1}
Specimen mounting	Packed powder pellet
Data collection mode	Reflection
Scan method	Step
$2\theta_{min}$	10°
$2\theta_{max}$	120°
$2\theta_{step}$	0.03°
Refinement	Refinement on F^2
Least-squares matrix	Full
R_p	0.052
R_{wp}	0.085
R_{exp}	0.020
$R_{(F)}$	0.108
Data points	3667
Profile function	Pseudo-Voigt
Parameters	119
Restraints	3
Constraints	26
Primary atom site location	Structure-invariant direct methods
Secondary atom site location	Difference Fourier map
Hydrogen site location	difference Fourier map
H-atom parameters	Constrained
W	$1/[\sigma^2(F_o^{\,2})+(0.0429P)^2]$ where $P = F_o^{\,2} + 2F_o^{\,2}V^3$
$(\Delta/\sigma)_{max}$	0.04
Background function	square polynomial for each range
Preferred orientation correction	$I_{corr} = I_{obs}/[1 + (\tau^2\text{-}1)\sin^2\varphi]^{1/2}$, axis (001), $\tau = 0.702$

The structure contained highly disordered solvent. Total solvent accessible volume / cell were 92.0%. Refinement of the solvent density was impossible and instead the contribution of the density to the reflection file was squeezed [9].

2.1.1 Crystal Structure Determinations of 2-formyl-3,6-bis(hydroxymethyl)phenyl benzoate

All measurements were made on an Oxford Gemini Ultra R diffractometer using graphite monochromatic Mo-K radiation (0.71073 Å), from a sealed Mo X-ray tube operating at 50 kV/40 mA [6]. The crystallographic data relevant to the structure determination was indexed on a PC using Fullprof 2k 5.80 software package [7] and was solved with the computer programs OLEX2 [8]. Crystal data, data collection and structure refinement details are summarized in Table 1.

2.2 Organic dry cell

A sheet of the starch-coated paper has been rolled flat into the inside of the metal cane, which serves as the anode. The organic paste with only enough moisture to allow current to flow was packed to the metal can so that the amount is about half inch less than the upper portion of the can. The paper was folded and the plastic seal was inserted onto the top end of the can. The carbon rod which serves as the cathode was firmly pushed straight from the hole in the seal. The cap of the rod and seal rested with each other. The entire cell assembly was cased in wax gently to prevent leakage. The circuit was connected to the cell. Recorded the charging, discharging and corresponding time taking place in the cell [10]. Figure II illustrates the typical charging/discharging characteristics of the cell for 1 h at 20º.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

MS, IR and X-ray diffraction are the most versatile and widely applied methods used for the characterization of the titled compound. MS, IR and X-ray spectra have

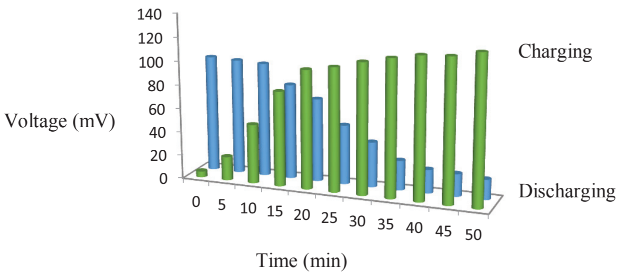


Figure 2: Charging and discharging of a cell.

been listed at the above. The data were compared with the literature in order to elucidate the binding mode in the compound. The IR spectrum exhibited solid absorption bands at 1740-1730 cm^{-1}, indicating esters stretching frequency of ν(C=O). Bands at 400-600 cm^{-1} are assigned to ν(M-O) and ν(M-Cl) respectively as well as ν(OH) band was also observed at 3460-3455 cm^{-1} [11]. In mass spectrogram the appearance of a molecular ion peaks has been assigned to monomeric nature. The ionization behavior was used to probe the molecular mass of compound. The peaks m/z (%) at 279, 205, 189, 175, 161, 145, 131, 117 and 71 revealed the loss of single ion at each step [12]. X-ray powder spectrum has shown the intense peaks with regard to the diffraction pattern. It was indexing that compound revealed an asymmetric trinuclear structure [13]. The detail of the structure solution has been described with the experimental and theoretical informatics methods. The crystal structure of 2-formylphenyl benzoate derivative bearing two hydroxymethyl on its phenyl has been determined. Bond lengths and angles are in the usual ranges except slight misplaced and long reported at the asymmetric centroid involving rotation of refined position. As depicted, compound crystallizes in the triclinic space group P1. The C-C, C-H, C-O and H-O mean distances are 1.415 Å, 1.099 Å, 1.344 Å and 0.930 Å respectively, which are within the normal ranges. Potential hydrogen bonds present in the geometry, by which the molecule is stabilized. There are C-H---O and O-H---O types of hydrogen bonds found in the packed structure. The key feature of the molecular packing is the formation of both intramolecular and intermolecular contacts. The oxygen atoms of the both carbonyl and hydroxyl groups are participated in hydrogen bonds formation respectively. It should be noted, secondary interactions between the rings routinely appear in the molecules. The aggregates of the aforementioned contacts resulted in three-dimensional layer of molecules [14]. The structures were solved by the direct methods using charge flipping and refined anisotropically with the olex2 refine refinement package using a gauss-newton minimization. The empirical absorption correction using spherical harmonics were applied. The cell e.s.d.'s are taken into account individually in the estimation of distances, angles and torsion angles. The threshold expression is used for calculating R-factors [15]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre UK as supplementary data, CCDC# 1575123 [16]. In this context, tilted compound might indeed be designed to evaluate its utility in the electrochemical dry cell. The electrolyte system in a cell consists of 2-formyl-3,6-bis(hydroxymethyl)phenyl benzoate paste in the immediate vicinity of each electrode. This cell was also tested to determine its voltage using one gram of paste and recorded 25 values of voltages (mV) with corresponding time (min). Cell was connected to the circuit, charged the cell for about 1 hr. and described the changes taking place in the cell. The reading of the cell while it was charging or discharging recorded at each interval of time that was 5 min. It has been noticed that cell is slowly charged to the applied voltage of "150 millivolts" and then cell delivered 150 millivolts for only the first few seconds of the discharge period. The majority of the voltage was less than 100 millivolts if the discharge of a charged cell was to continue and remaining energy was still in the cell. Designed cell is a device in form of electric charge and store much smaller amount of energy around 100 millivolts smaller. The development work is a somewhat new technology and ongoing to improve charge/discharge capacity [17]. The paste is mixed with carbon powder to increase the electrical conductivity. The electrodes are made of zinc and carbon (graphite), with a paste of acidic materials between them serving as the electrolyte. Graphite is the non-corrode conductor material surrounded by MnO_2 acts as the positive electrode that collects electrons coming from the anode portion of the cell to return to the cathode portion of the cell. The metal cylinder (Zn) serve as anode. Zinc is nontoxic and cheap, therefore, the use of zinc catalysts is convenient from sustainability aspects. In a normally functioning cell, the only reactions that should be occurring are the half-cell reactions on the electrodes [18-19]. At the anode, zinc is oxidized and transport between the electrodes and the electrolyte as Zn^{+2} ions. The anode half-reaction is as follows,

These electrons are transferred to the paste and herein, wish to propose a general methodology for the Zn(II) catalyzed oxidation of biphenol units to the corresponding aldehyde and acid. To the best of our knowledge, the mechanism of this assay is well recognized in the literature. The reaction of low-valent

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

Figure 3: Anode half cell reaction.

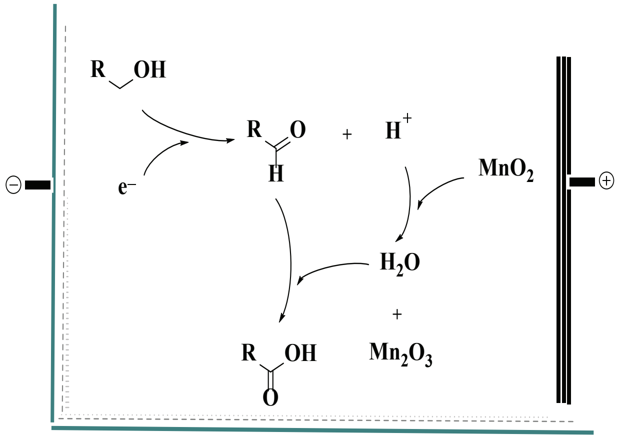


Figure 4: The reaction occurs within the moist paste.

zinc with alcohol groups probably followed a rival way. The zinc here is hydrogen acceptor in a multistep electron-transfer process. The zinc metal deveplop force after sometime since zinc container develop hole. This sleeve will get thinner as the zinc oxidizes and the cell will no longer be able to conduct electricity once the zinc sleeve is completely gone. So to prevent leakage the zinc container is surrounded by iron coating (hard board). However, the organic paste is oxidatively destroyed at the anode [20]. If the cell is used continuously for a long time polarization eventually sets in due to accumulation of hydrogen on carbon rod and the action stops. When allow to rest the accumulated hydrogen is oxidized to water by the MnO_2 and the cell is again ready for use. When cell was connect the two terminals with wire, a circuit is formed. Electrons will flow through the wire and a current of electricity is produced. Inside the cell, a reaction between chemicals take place. But the reaction takes place only if there is a flow of electrons [21]. The reaction occurred within the paste is shown in Figure 4.

Cell can be stored for a long time and still work because the chemical process doesn't start until the electrons flow from the negative to the positive terminals through a circuit. The top of the cell is covered by a conductive plate so that the carbon rod can make contact with the positive terminal on the outside of the cell. A non-conductive tube forms the sides of the cell and ensures that there is no direct electrical contact between the carbon rod and the zinc sleeve. It has been noticed that a few catalytic systems based on this general concept have been designated in the literature, hence this is still a very open subject. Inside the cell electrons are pushed by the chemical reaction toward the positive end creating a potential difference. The electrolyte in the cell keeps lone electrons from going straight from the anode to the cathode within the cell is responsible for the production of the electricity. When the terminals are connected with a conductive wire, electrons flow from anode to cathode. Designed dry cell is that cell in which reaction occurs only once after use over a period of time and cell becomes dead and cannot be reused. It cannot be recharged and is discarded after they run down when all the chemicals are used up.

4 Conclusions

In this present, organic dry cell based on the standard principle is designed. The electrolyte system in a cell consists of organic paste and we envision from our potential results. A search of the cambridge structural database gave no match for the title compound. $Olex_{2\text{-}1.2}$ 2017 solve structure solution program was used to solve the crystal. In this research, article has attempted information specific to the electrochemical application of titled compound. User with an interest is extremely encouraged for further research with the utilization of organic compounds.

Conflict of interest: Authors state no conflict of interest.

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