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Synthesis and Crystal Structure of 7,8-dihydroxy-2,4-dimehyl Chromylium Perchlorate using Hirshfeld Surface Analysis

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The title compound, $C_{11}H_{11}ClO_7$, crystallizes in the monoclinic crystal system and space group $P2_1/n$ with cell parameters a = *6.8920(4)Å,* b = *18.5260(15)Å,* c = *9.9480(8)Å,* β = *106.420(5)°,* V = *1218.37(16)Å^3 for* Z = *4. The structure exhibits both intra and inter-molecular hydrogen bonds of the type O—H... O and C—H... O.*

Keywords chromylium; crystal structure; hydrogen bond

Introduction

Chromylium is a structurally novel compound. Chromylium salts were first prepared by Decker, Fellenberg, Perkin, and Robinson [1–3]. The Chromylium salts show antimicrobial activity [4]. They are strong electrolytes as shown by their conductivity in acetonitrile and dipole moment measurements [5,6]. Several Benzopyrillium perchlorates are useful sensitizers for conventional organic photoconductors [7]. Bulow and Wagner have reported the condensation of resorcinol, pyrogallol and phloroglucinol with acetyl acetone using hydrogen chloride in glacial acetic acid which results in the formation of the corresponding 2,4-dimethylchromylium chloride [8].

Synthesis and Method of Crystallization

To a mixture of pyrogallol (0.05 mol) and acetyl acetone (0.05 mol), perchloric acid (70%, 7.5 ml) was added slowly with external cooling. It was cooled in an ice-bath. Dry hydrogen chloride gas was bubbled through the reaction mixture for 1–2 h, with the result it became dark reddish in color. It was kept overnight at room temperature and then diluted with excess of dry ether, then the colored precipitate was filtered and washed with dry ether, dried, and crystallized from glacial acetic acid.

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Table 1. Crystal data and structure refinement table

CCDC	983102
Empirical formula	$C_{11}H_{11}ClO_7$
Formula weight	290.65
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Spacegroup	$P2_1/n$
Cell dimensions	A = 6.8920(4) Å
	B = 18.5260(15) Å
	C = 9.9480(8) Å
	$\beta = 106.420(5)^\circ$
Volume	1218.37(16) Å^3
Z	4
Density(calculated)	1.585 Mg/m^3
Absorption coefficient	0.341 mm^{-1}
F_{000}	600
Crystal size	0.3 × 0.25 × 0.25 mm
θ range for data collection	2.40° to 25°
Index ranges	$-7 \leq h \leq 7$
	$-22 \leq k \leq 21$
	$-11 \leq l \leq 11$
Reflections collected	3470
Independent reflections	1895 [$R_{int} = 0.0169$
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1895 / 0 / 175
Goodness-of-fit on F^2	1.143
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0554$, w$R2 = 0.1603$
R indices (all data)	$R1 = 0.0614$, w$R2 = 0.1729$
Extinction coefficient	0.096(15)
Largest diff. peak and hole	0.460 and −0.599 e.Å^{-3}

7,8-dihydroxy-2,4-dimehyl chromylium perchlorate salt (1.0 g) was taken in 25–35 ml glacial acetic acid. It was heated for 10–15 min till it got dissolved. 0.5 g charcoal was added to the mixture and the solution was heated for more than 2–3 min. The solution was filtered while hot through Whatmann 41 filter paper. The solution was kept in a stopper conical flask slightly opened. The crystals were grown by thin film evaporation.

Crystal Structure Determination

A single crystal of the title compound with dimensions 0.30 × 0.25 × 0.25 mm was chosen for the X-ray diffraction study. The data were collected on a DIPLabo Image Plate system equipped with a normal focus, 3 kW sealed X-ray source (graphite monochromated MoK $_\alpha$). The crystal to detector distance was fixed at 120 mm with the detector area of 441 × 240 mm^2. Thirty-six frames of data were collected at room temperature by the oscillation method. Each exposure of the image plate was set to 400 s. Successive frames

Table 2. Atomic coordinates and equivalent thermal parameters of the nonhydrogen atoms

Atom	x	y	z	U_{eq}
O1	0.2427(3)	0.17700(9)	0.51669(2)	0.0418(5)
C2	0.3647(4)	0.18857(1)	0.4363(3)	0.0437(7)
C3	0.3331(5)	0.15380(2)	0.3102(3)	0.0477(7)
C4	0.1724(5)	0.10591(1)	0.2626(3)	0.0455(7)
C5	0.0392(4)	0.09519(1)	0.3455(3)	0.0406(7)
C6	−0.1319(5)	0.04933(1)	0.3097(3)	0.0471(7)
C7	−0.2497(4)	0.04226(1)	0.3988(3)	0.0480(7)
C8	−0.2037(4)	0.07958(1)	0.5263(3)	0.0435(7)
C9	−0.0375(4)	0.12525(1)	0.5655(3)	0.0425(7)
C10	0.0794(4)	0.13234(1)	0.4736(3)	0.0377(6)
C11	0.5287(5)	0.23995(2)	0.4985(4)	0.0550(8)
C12	0.1448(6)	0.06698(2)	0.1264(3)	0.0630(9)
O13	−0.3263(3)	0.06990(1)	0.6095(2)	0.0563(6)
O14	−0.0007(3)	0.16115(1)	0.6896(2)	0.0559(6)
Cl15	0.5214(1)	0.14498(4)	0.90272(8)	0.0526(4)
O16	0.6950(5)	0.14292(2)	0.8535(3)	0.1011(1)
O17	0.3988(5)	0.08447(2)	0.8549(4)	0.1117(1)
O18	0.4041(5)	0.20626(2)	0.8397(4)	0.1026(1)
O19	0.5809(6)	0.1537(2)	1.0484(3)	0.1035(1)

$U_{eq} = (1/3)$.
$\Sigma_i \Sigma_j U_{ij}(a_i^* \cdot a_j^*)(a_i \cdot a_j)$.

were scanned in steps of 5° per minute with an oscillation range of 5°. Image processing and data reduction were done using Denzo [9]. The reflections were merged with Scalepack [10]. All the frames could be indexed using a monoclinic lattice. Absorption correction was not applied. The structure was solved by direct methods using SHELXS-97 [11].

Least-squares refinement using SHELXL-97 [12] with isotropic temperature factors for all the nonhydrogen atoms converged the residual R1 to 0.0614. Subsequent refinements

Table 3. Bond Lengths (Å)

Atoms	Length	Atoms	Length
O1-C2	1.332(3)	C7-C8	1.400(4)
O1-C10	1.364(3)	C8-O13	1.351(3)
C2-C3	1.371(4)	C8-C9	1.388(4)
C2-C11	1.474(4)	C9-O14	1.362(3)
C3-C4	1.394(4)	C9-C10	1.386(4)
C4-C5	1.411(4)	Cl15-O19	1.399(3)
C4-C12	1.498(4)	Cl15-O17	1.403(3)
C5-C10	1.405(4)	Cl15-O16	1.416(3)
C5-C6	1.415(4)	Cl15-O18	1.431(3)
C6-C7	1.367(4)		

Table 4. Bond Angles(°)

Atoms	Angle	Atoms	Angle
C2-O1-C10	120.9(2)	O13-C8-C7	117.9(2)
O1-C2-C3	120.6(2)	C9-C8-C7	120.9(3)
O1-C2-C11	113.0(3)	O14-C9-C10	123.9(2)
C3-C2-C11	126.3(3)	O14-C9-C8	118.7(3)
C2-C3-C4	121.0(3)	C10-C9-C8	117.4(3)
C3-C4-C5	118.5(3)	O1-C10-C9	115.6(2)
C3-C4-C12	120.0(3)	O1-C10-C5	121.1(2)
C5-C4-C12	121.6(3)	C9-C10-C5	123.3(2)
C10-C5-C4	117.8(3)	O19-Cl15-O17	114.5(2)
C10-C5-C6	117.3(3)	O19-Cl15-O16	109.4(2)
C4-C5-C6	124.8(3)	O17-Cl15-O16	110.4(2)
C7-C6-C5	120.0(3)	O19-Cl15-O18	109.0(2)
C6-C7-C8	121.1(3)	O17-Cl15-O18	105.9(2)
O13-C8-C9	121.2(3)	O16-Cl15-O18	107.3(2)

were carried out with anisotropic thermal parameters for nonhydrogen atoms and isotropic temperature factors for the hydrogen atoms which were placed at chemically acceptable positions. The hydrogen atoms were allowed to ride on their parent atoms. After eight cycles of refinement, the residual converged to 0.0554. The details of crystal data and refinement are given in Table 1.* Table 2 gives the atomic coordinates and equivalent thermal parameters of the nonhydrogen atoms. Tables 3 and 4 give the list of bond lengths and bond angles, respectively, which are in good agreement with the standard values. The ORTEP of the molecule with thermal ellipsoids drawn at 50% probability is shown in Fig. 2.

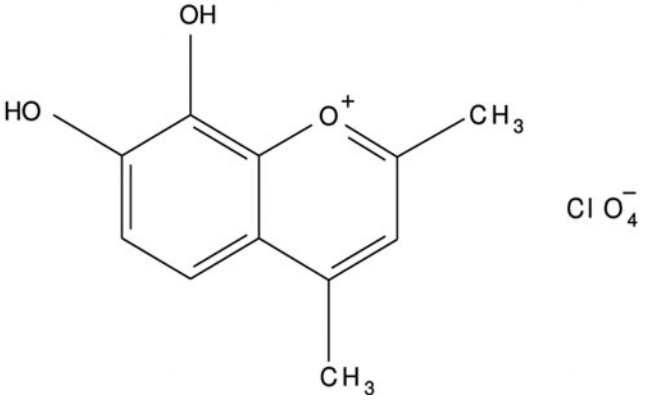

Figure 1. Schematic diagram.

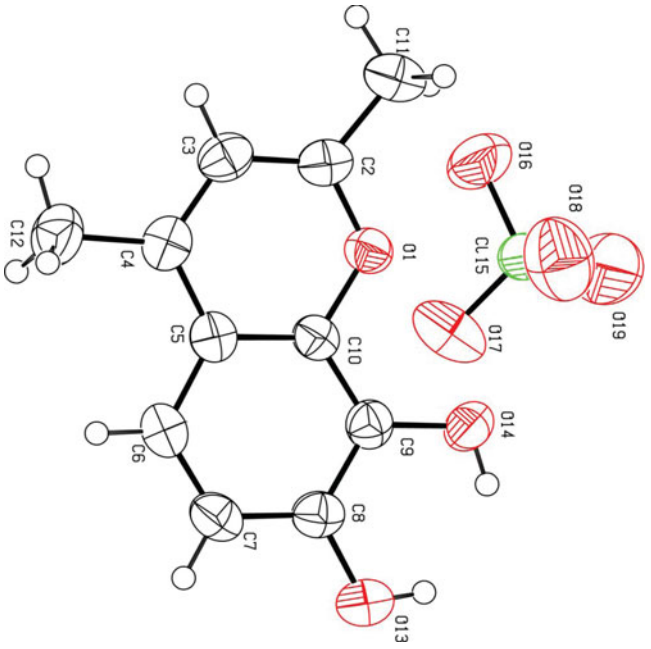

Figure 2. ORTEP of the molecule at 50% probability.

The title compound shows planar conformation. The dihedral angle between the least squares planes O1-C2-C3-C4-C5-C10 and C5-C6-C7-C8-C9-C10 is 0.29(1)°. Total puckering amplitude Q for ten-membered ring O1-C2-C3-C4-C5-C6-C7-C8-C9-C10 is 0.026(3)Å. The torsion angle about C3-C4-C5-C6 is 178.9(3)°, while that of O13-C8-C9-C10 is −179.6(2)°, both shows −anti-periplanar conformation, respectively. The molecule exhibits inter and intramolecular hydrogen bonds of the type O—H . . . O and C—H . . . O. The intermolecular hydrogen bonds O13-H13 . . . O16, O14-H14 . . . O16 and C11-H11A . . . O16 have lengths of 2.746(4)Å, 3.017(4)Å and 3.194(5)Å and angles of 155°, 168° and 139°, respectively, with the symmetry codes $-1+x, y, z$ and $-1/2+x$, $1/2-y, -1/2+z$.

Intramolecular hydrogen bond O14-H14 . . . O13, has a length of 2.742(3)Å and an angle of 115°. A packing of the molecules viewed down a-axis shows one-dimensional snake shaped chain in Fig. 3.

Hirshfeld Surface Analysis

The intermolecular interactions of the title compound are quantified using Hirshfeld surface analysis. This approach is a graphical tool for visualization and understanding of intermolecular contacts [13]. Here, we estimate the intermolecular contacts, which are shown in Fig. 4. Two-dimensional fingerprint plots from Hirshfeld surface analyses illustrates the difference between the intermolecular interaction patterns and the relative contributions to the Hirshfeld surface (in percentage) for the major intermolecular contacts

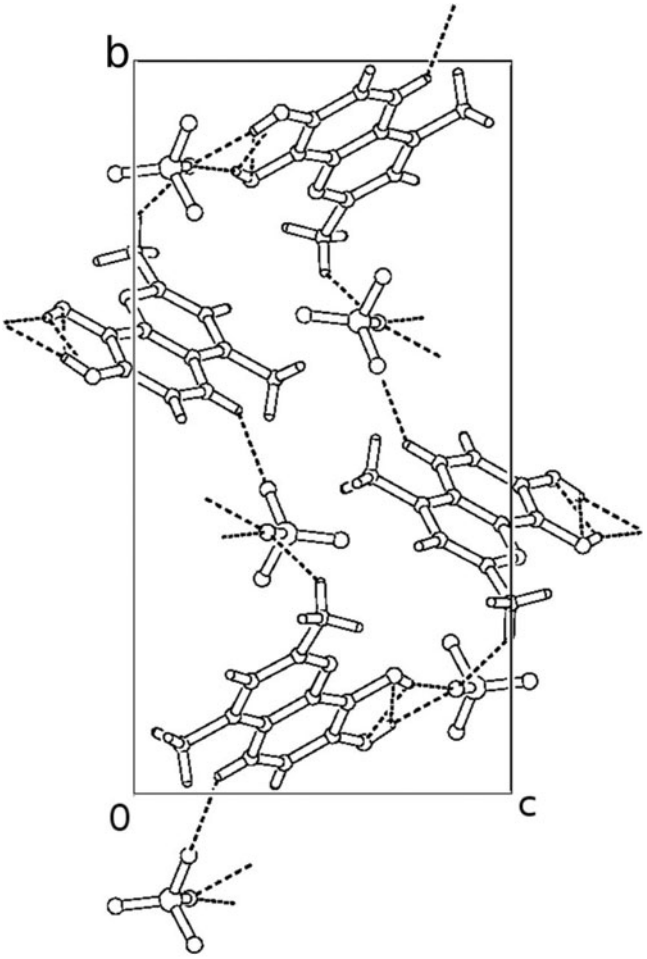

Figure 3. Packing of the molecules down the a axis. The dashed lines represent the hydrogen bonds.

associated with the title compound. The contribution of intercontacts to the Hirshfeld surfaces are, O . . . H(26.6%), H . . . H(23.2%), C . . . H(6.5%) and others (O . . . O, O . . . H, C . . . C, C . . . O, H . . . O; 43.7%). These intercontacts are highlighted by conventional mapping of d_{norm} on molecular Hirshfeld surfaces are shown in Fig. 5. The red spots over the surface indicate the intercontacts involved in hydrogen bond. Importantly, H . . . H bonding appears to be a major contributor in the crystal packing, whereas the O . . . H and C . . . H plots also reveal the information of intermolecular hydrogen bonds. In Fig. 6, the shape index and curvedness shows characteristic packing arrangements and the ways in which adjacent molecules contact one another. The shape index surface clearly shows that the two sides of the molecules are involved in same contacts with neighboring molecules and curvedness plots show flat surface patches characteristic of planar stacking.

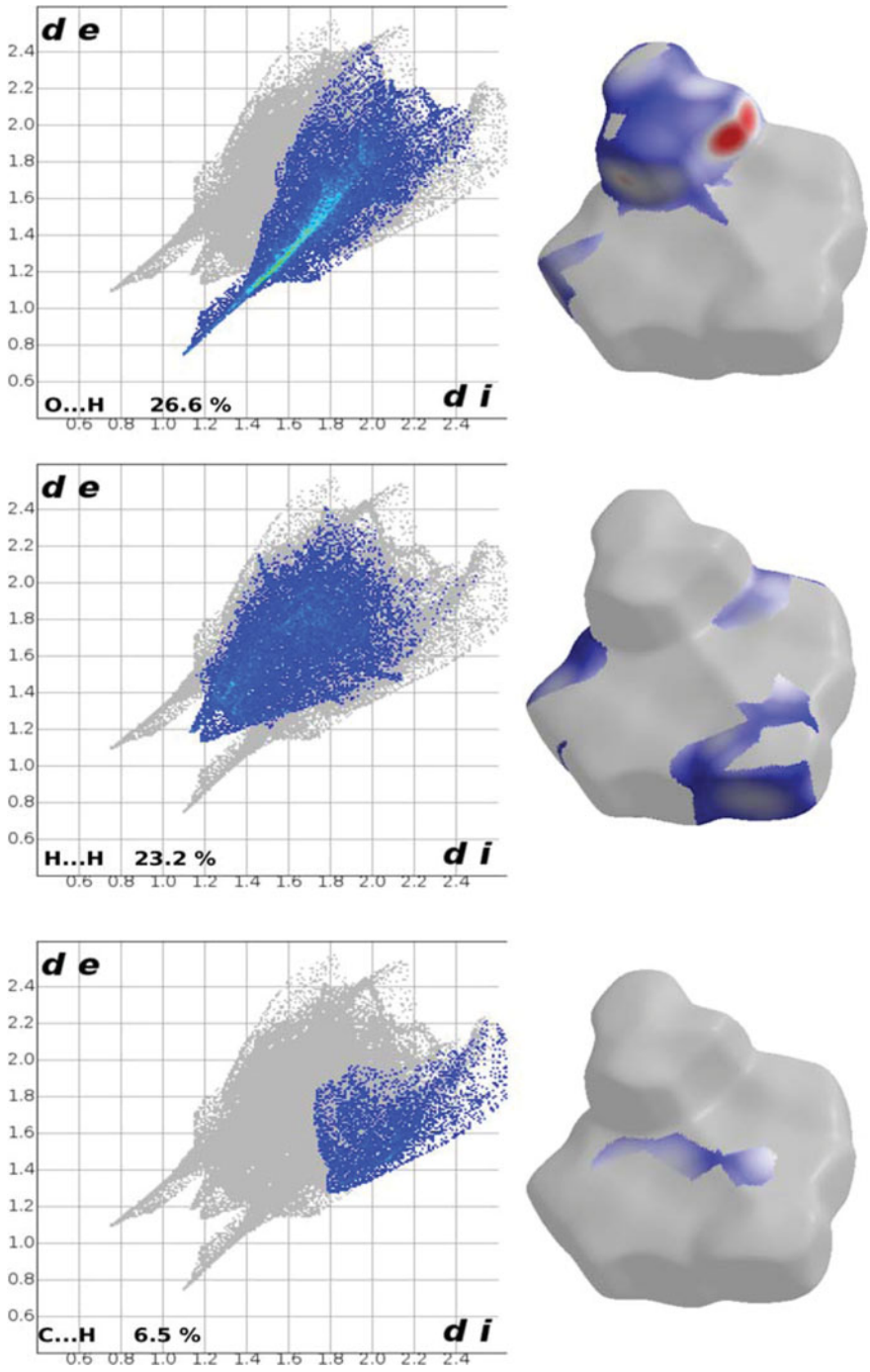

Figure 4. Fingerprint of the title compound, O . . . H, H . . . H and C . . . H. The outline of the full fingerprint is shown in gray. di is the closest internal distance from a given point on the Hirshfeld surface and de is the closest external contacts with percentage of various intermolecular contacts contributed to the Hirshfeld surface. Surfaces to the right highlight the relevant surface patches associated with specific contacts.

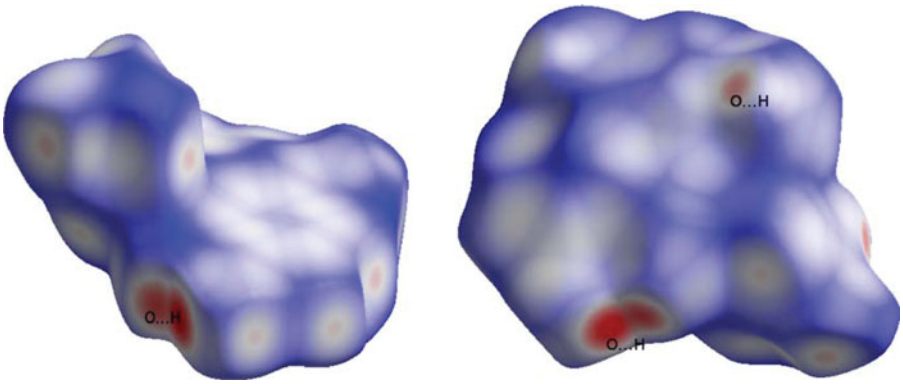

Figure 5. d_{norm} mapped on Hirshfeld surface for visualizing the intercontacts of the title compound. Color scale in between -0.18 au(blue) to 1.4 au (red).

*‘‘CCDC 983102 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033. email: deposit@ccdc.cam.ac.uk”

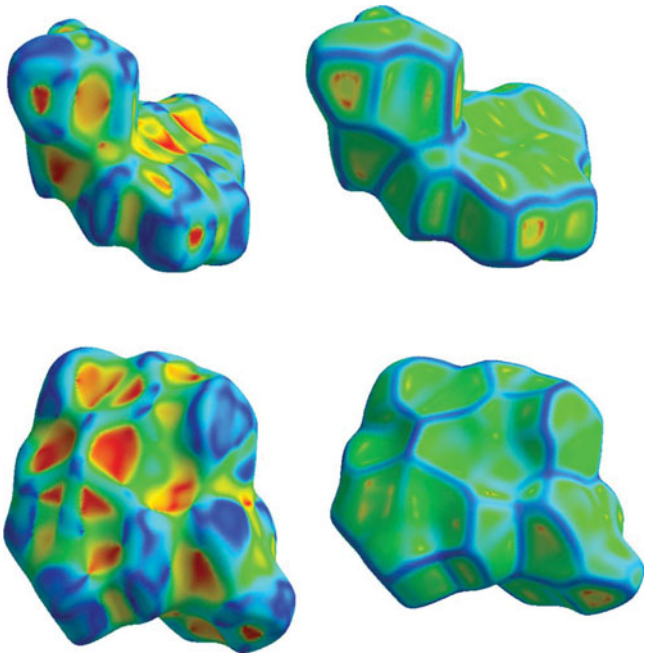

Figure 6. Front and back views of the Hirshfeld surface for title compound mapped with shape index and curvedness.

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