

## Article

# Third Unique Polymorph of bis(2,9-Dimethyl-1,10-phenanthroline)-Copper(I) tetrafluoroborate, [Cu(dmp)<sub>2</sub>](BF<sub>4</sub>)

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## Abstract

Polymorphic behavior has significant consequences in solid-state properties relevant to functional materials and pharmaceutical applications. This study reports the single-crystal X-ray structure of a new third unique polymorph of the photoluminescent compound [Cu(dmp)<sub>2</sub>](BF<sub>4</sub>) (dmp = 2,9-dimethyl-1,10-phenanthroline). A detailed analysis of how this new polymorph compares with the two previously reported polymorphs was carried out including intramolecular metrics ( $\tau^4$ , twisting, flattening, rocking measures) and intermolecular differences ( $\pi$ -stacking, Hirshfeld surfaces). The new polymorph reported here has larger twisting and flattening distortions from an idealized tetrahedral geometry and the largest displacement of Cu from one dmp plane than the other polymorphs. This new polymorph also exhibits enhanced  $\pi$ -stacking that leads to more dense packing than previous reported polymorphs. Hirshfeld surface comparisons are consistent with a larger percentage of C...C short contacts and lower percentage of C...H contacts present in this new polymorph. The variability of intra- and intermolecular differences within this family of three polymorphs compared demonstrates the large degree of flexibility of both the coordination sphere and packing, even with the expected rigid planar bis-bidentate dmp binding to copper. As the polymorphs each show unique inter- and intramolecular features, differences in solid-state properties including solid-state photoluminescence are expected. This demonstrates the importance of phase purity in the construction of solid-state device applications.

**Keywords:** polymorphs; tetrahedral distortions;  $\tau^4$ ;  $\pi$ -stacking; Hirshfeld surface

## 1. Introduction

Polymorphs can be described as unique structural packing arrangements of identical chemical compositions. Small differences in the energy landscape of solid-state structures with different intra- and intermolecular features allow for these unique patterns to be characterized [1]. Access to different polymorphs may be the result of different crystallization conditions (solvents used, methods of crystallization such as vapor diffusion, layering of solutions, melt crystallization, evaporation, sublimation), changes in temperature or pressure, time, or others. Two primary considerations for the access of different polymorphs are the thermodynamic vs. kinetic regimes under which crystalline materials form [2]. Crystallization under thermodynamically controlled conditions allows for lower free energy structures to form, while kinetically controlled conditions allow for the formation of higher free energy polymorphs [3]. For solution and melt crystallization, higher crystallization temperatures have been shown to promote thermodynamically controlled polymorph



Academic Editor: Yael Diskin-Posner

Received: 12 July 2026

Revised: 23 July 2026

Accepted: 27 July 2026

Published: 28 July 2026

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formation [4], while lower temperatures often yield kinetic forms [5]. Solvent polarity can also play a strong role in guiding polymorph formation [6,7].

Crystallographic characterization is sometimes used solely for verification of intramolecular bonding considerations. As more exquisite control of solid-state properties is now possible, detailed analysis of intermolecular features is of increasing interest. However, when crystal structure analysis is used solely for connectivity verification, further studies to pursue polymorphs are often not sought after though they may exist. Unless systematic investigations are carried out to seek new polymorphs or another obvious physical property such as color differences between crystals of the same compound is observed [8], new packing arrangements are often discovered solely by accident or simply go unnoticed and uncharacterized. The solid-state physical properties of different polymorphs, however, can vary significantly as molecular shape and packing influence solubility, melting point, hygroscopicity, stability, color, solid-state photoluminescence and others. As such, study of how polymorphs differ can provide information to help to better engineer the desired properties of functional solid-state materials [9] and pharmaceutical compounds [10].

A small, but significant, fraction of crystallographically characterized molecular compounds is known to exhibit polymorphic behavior. A study in 2022 of the Cambridge Crystallographic Database (CSD) estimated the total polymorph occurrence at 4.2% (of the then 1.2 million structures) [10]. This rate of occurrence is likely an overestimation. A careful study in 2005 of high-quality reliably verified polymorphs indicates only an estimate of 0.5% of all CSD structures as having at least two polymorphs [11]. The CCDC [12] reports that as of 2026, only 1% of all Refcode families are polymorph families. A 1998 [13] comparison of polymorphs indicates the prevalence of structurally characterized metal–organic polymorphs at half that of purely organic compounds, while a 2013 analysis estimates this ratio at 3:2 [14]. This same study points out that the lower occurrence of reported polymorphs of coordination or metal–organic compounds compared to organics may have more to do with the application of the compounds than an inherent likelihood for metal–organics to adopt polymorphic forms. This potential reasoning is consistent with McCrone’s statement regarding polymorphs: ‘the number of polymorphic forms for a given compound is proportional to the time and money spent in research on that compound’ [15]. As organic compounds of pharmaceutical interest have attracted intense study by drug companies including high-throughput screening to identify new polymorphs for patent protections, it is of no surprise that organic polymorphs identified are of higher occurrence than metal–organics.

A closer inspection of polymorph families indicates a decreasing rate of occurrence for compounds with increasing numbers of structurally characterized polymorphs of the same compound. To date, the molecular compound ROY (5-methyl-2-((2-nitrophenyl)amino)thiophene-3-carbonitrile) has the largest number of characterized polymorphs at 14 [16]. In a 2011 study of the CSD of only organic polymorphs with high-quality structures and  $Z' = 1$ , 89% of these compounds had exactly two polymorphs characterized, 9% had three polymorphs, 1% had four polymorphs, and <1% composed all molecules with five or greater unique polymorphs [17].

Since the first report of the synthesis and room temperature solution photoluminescent coordination compound  $[\text{Cu}(\text{dmp})_2](\text{BF}_4)$  [18,19], interest in the unique photophysical properties of related bis-diimine systems have garnered wide attention [20]. Applications involving thermally activated delayed fluorescence, as these materials are now known to employ, include optical technologies such as OLEDs [21], sensor devices [22] photocatalysis [23], and dye-sensitized solar cells [24]. Sterically demanding methyl groups in the 2,9-positions of the phenanthroline ligands prevent large flattening distortions from tetrahedral geometry in the excited state that can lead to increased non-radiative decay

pathways resulting in lower quantum yields of emission [25]. Studies by Coppens [26] demonstrate that molecular distortions of the  $[\text{Cu}(\text{dmp})_2]^+$  coordination sphere lead to significant effects on solid-state emission lifetimes. Variations in the counter anion and solvates have also been shown to dramatically affect the distortions observed in  $[\text{Cu}(\text{dmp})_2]^+$  cations in a large series of structures [27]. In particular, rocking and flattening distortions from ideal geometries of the tetrahedral copper(I) coordination environment can cause significant twisting toward a more flattened square planar-type Cu(II) geometry, leading to red-shifted emission wavelengths. Furthermore, solid state luminescence quenching in salt  $[\text{Cu}(\text{dmp})_2]^+$  cations due to intermolecular energy transfer has been shown to correlate with the energy gap between luminescing donor and quenching acceptor [27]. More recent investigations have quantified photophysical changes induced by crystal lattice-induced stress compared with those carried out on  $[\text{Cu}(\text{dmp})_2](\text{PF}_6)$  [28]. By quantifying molecular distortions at this  $[\text{Cu}(\text{dmp})_2]^+$  chromophore, observations indicate that polymorphic structures of this cation (and by extension, related materials) have measurable differences in solid-state photophysical properties. Thus, careful polymorph selection and design of materials whose solid-state properties (such as photoluminescence) are employed in their uses must be considered.

This study of a new structurally characterized polymorph of  $[\text{Cu}(\text{dmp})_2](\text{BF}_4)$  and comparison with the two previously reported polymorphs intends to shed light on the flexibility of this cation (even for the same salt) and the variety of intra-and intermolecular motifs this compound can adopt in the crystalline solid state.

## 2. Materials and Methods

### 2.1. General Considerations

The starting material  $[\text{Cu}(\text{NCCH}_3)_4](\text{BF}_4)$  was prepared according to previously reported methods [29]. The ligand 2,9-dimethyl-1,10-phenanthroline (dmp) was purchased from Sigma Aldrich (St. Louis, MO, USA). A Formtech Scientific FTS-1000 mixer mill (Hamilton, ON, Canada) was used with 15 mL stainless steel jars and two stainless steel balls of diameter 4 mm.

### 2.2. Sample Preparation

In an agate mortar, colorless  $[\text{Cu}(\text{NCCH}_3)_4](\text{BF}_4)$  (0.098 g, 0.31 mmol) and colorless dmp (0.130 g, 0.63 mmol) were combined and ground with a pestle for a total of 10 min. Within seconds, orange solid appears in the ground mixture. After each 1 min, the solids were scraped from the walls of the mortar using a spatula as the solids became sticky as the reaction proceeded. After 10 min of grinding, the solid became less sticky and increasingly like a powder. All orange solids were scraped from the mortar to remove, and the solid was dried overnight in vacuo to obtain 0.16 g (90%) of **1**,  $[\text{Cu}(\text{dmp})_2](\text{BF}_4)$ . No further purification was needed. Spectroscopic data including IR and NMR [30] were identical with previous reports of this complex prepared in a solution reaction. Nearly identical results were obtained by grinding using a mixer mill at 1800 rpm for 15 min, followed by drying in vacuo. After drying the solid product in each method, no evidence of acetonitrile was present by NMR or IR. Crystals of **1a** suitable for X-ray diffraction, red plates, were obtained by vapor diffusion of diethyl ether into a concentrated solution of methanol.

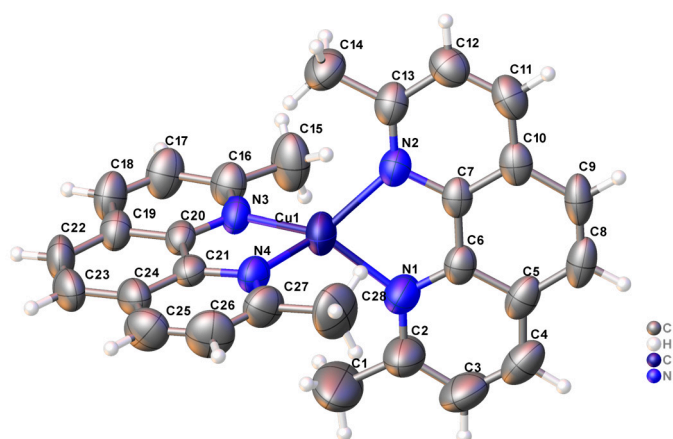
### 2.3. Single-Crystal X-Ray Diffraction

Table S1 contains crystal data, collection parameters, and refinement criteria for the crystal structure of **1a**. A suitable crystal was selected and mounted using a Mitigen micro-mount. Crystallographic data were collected at 293(2) K with a graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Rigaku XtaLAB mini diffractometer (Tokyo, Japan)

using ChrysalisPro software v43.141a [31]. Using Olex2 v1.5 [32], the structure was solved with the SHELXS-1997 [33] structure solution program using direct methods and refined with the SHELXL 2019 [34] refinement package using least squares minimization. The intensity data were corrected for absorption and decay using the SCALE3 ABSPACK scaling algorithm [31]. All non-hydrogen atoms were refined with anisotropic displacement parameters. To adequately model positional disorder in the  $\text{BF}_4^-$  anion, two similar positions (B1, F1–F4 and B2, F5–F8) were located and freely refined with occupancy percentages of 38%/62% for B1, F1–F4 and B2, F5–F8 respectively. The thermal parameters of B1 and B2 were constrained to be identical and atoms F1–F8 anisotropic thermal parameters were restrained to be approximately isotropic (ISOR). All hydrogen atoms were refined using the riding model.

### 3. Results and Discussion

During the course of studying mechanochemical preparation of bis-diimine copper(I) complexes,  $[\text{Cu}(\text{dmp})_2](\text{BF}_4)$  was prepared and crystallized. Though our crystallization conditions were not identical to previous reported polymorphs (Refcode IPICOZ [27] **1b**– $\text{CH}_3\text{CN}$  evaporation; Refcode IPICOZ01 [35] **1c**– $\text{CH}_3\text{OH}$ /water), unexpectedly, a new polymorph **1a** was discovered and characterized by single-crystal X-ray diffraction. A thermal ellipsoid diagram of the new polymorph **1a** is shown in Figure 1.



**Figure 1.** Thermal ellipsoid diagram of **1a** (50% probability ellipsoids).  $\text{BF}_4^-$  anions omitted for clarity.

Previous work has demonstrated the flexibility in the coordination sphere and packing of unsolvated  $[\text{Cu}(\text{dmp})_2]\text{X}$  complexes ( $\text{X} = \text{BF}_4^-$ ,  $\text{PF}_6^-$  [26],  $\text{NO}_3^-$  [30],  $\text{CF}_3\text{COO}^-$  [36], and others) as well as the ability to crystallize as a range of several solvates of these salts. As such, a systematic comparison of intra- and intermolecular features of the new polymorph reported here with the two previous structures of this compound of this study was carried out with the goal of gaining insight into this rich polymorphic landscape.

#### 3.1. Crystallographic Data Comparison of Polymorphs

Table 1 summarizes crystallographic data for the new polymorph **1a** as well as comparison with the two previously reported polymorphs **1b** and **1c**.

In each structure of the three polymorphs, all cations and anions lie on general positions. At least two interesting observations can be made from the unit cell and space group information. For each of the polymorphs, the data collection was carried out at different temperatures. The report of **1b** notes that no phase changes in their crystal sample occurred upon cooling to 90 K. While both **1a** and **1c** are monoclinic, **1b** is orthorhombic but **1c** has a  $Z' = 2$  with two unique  $[\text{Cu}(\text{dmp})_2]^+$  cations and two unique  $\text{BF}_4^-$  anions. The monoclinic unit cell angle  $b$  for **1c** ( $90.103(4)^\circ$ ) is quite close to that of an orthorhombic cell. Close

comparison of the unit cells of **1b** and **1c** suggest a crystallographic supercell-to-sublattice reduction from polymorph **1c** to polymorph **1b** involving the transformation matrix  $P$ :

$$P = \begin{pmatrix} 0 & 0 & 0.5 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

**Table 1.** Crystallographic data comparison of three polymorphs of  $[\text{Cu}(\text{dmp})_2](\text{BF}_4)$ .

| Polymorph                | <b>1a</b> | <b>1b</b>     | <b>1c</b> |
|--------------------------|-----------|---------------|-----------|
| CCDC Number              | 2571612   | 228941        | 729154    |
| Temperature (K)          | 293       | 173           | 90        |
| Space Group              | $P 2_1/n$ | $P 2_12_12_1$ | $P 2_1/c$ |
| $a$ (Å)                  | 13.308(1) | 11.7315(2)    | 12.514(3) |
| $b$ (Å)                  | 10.457(1) | 12.0990(2)    | 18.018(4) |
| $c$ (Å)                  | 17.646(2) | 18.0211(2)    | 23.063(5) |
| $\alpha$ (°)             | 90        | 90            | 90        |
| $\beta$ (°)              | 93.87(1)  | 90            | 90.103(4) |
| $\gamma$ (°)             | 90        | 90            | 90        |
| $V$ (Å <sup>3</sup> )    | 2471.1(5) | 2557.90(7)    | 5200(2)   |
| $Z, Z'$                  | 4, 1      | 4, 1          | 8, 2      |
| $d$ (g/cm <sup>3</sup> ) | 1.524     | 1.472         | 1.448     |

The accompanying unit cell volume change and packing changes upon unit cell transformation when data is collected at a lower temperature (**1b** = 173 K vs. **1c** = 90 K) however leads to a decrease in density (**1b** = 1.472 g/cm<sup>3</sup> vs. **1c** = 1.448 g/cm<sup>3</sup>). As symmetry-lowering is more common upon cooling, the transformation from the higher symmetry orthorhombic (**1b**) cell to lower symmetry monoclinic unit cell (**1c**) in this case is at least partially offset by the decrease in  $Z'$  from 2 to 1, where two unique conformations of the  $[\text{Cu}(\text{dmp})_2]^+$  cations are present in the asymmetric unit of **1c**. The 293 K data collection structure **1a** also has the unexpectedly highest density of these three polymorphs (**1a** = 1.524 g/cm<sup>3</sup>). Closer inspection of intramolecular coordination geometries and intermolecular packing of these three polymorphs are needed to understand these observations.

The related salt  $[\text{Cu}(\text{dmp})_2](\text{ClO}_4)$  with the structurally similar tetrahedral perchlorate anion also demonstrates rich polymorphic behavior that resembles the polymorphic behavior of  $[\text{Cu}(\text{dmp})_2](\text{BF}_4)$ . Three polymorphs of  $[\text{Cu}(\text{dmp})_2](\text{ClO}_4)$  are reported: monoclinic [37,38], triclinic [39], and orthorhombic [40] (Table S2). The monoclinic polymorph of  $[\text{Cu}(\text{dmp})_2](\text{ClO}_4)$  (with data collected at both 293 K and 100 K) is isostructural with the new polymorph in this report, **1a**. Stability of the monoclinic polymorph at both 293 K and 100 K may suggest this particular polymorphic arrangement is unlikely to undergo temperature-induced polymorph changes in this range. Both of these reported monoclinic structures of  $[\text{Cu}(\text{dmp})_2](\text{ClO}_4)$  also have the highest density of the three polymorphs reported, akin to **1a** amongst the three  $[\text{Cu}(\text{dmp})_2](\text{BF}_4)$  polymorphs. The orthorhombic polymorph of  $[\text{Cu}(\text{dmp})_2](\text{ClO}_4)$  is isostructural with polymorph **1b** of  $[\text{Cu}(\text{dmp})_2](\text{BF}_4)$ . The triclinic polymorph of has no polymorphic analog yet described for  $[\text{Cu}(\text{dmp})_2](\text{BF}_4)$ .

### 3.2. Intramolecular Coordination Geometry Comparison of Polymorphs

Table 2 summarizes metrics that describe twisting, flattening, and rocking measures of the bis-dmp coordination at each unique copper(I) center.

**Table 2.** Coordination geometry distortion parameters comparison of three polymorphs of [Cu(dmp)<sub>2</sub>](BF<sub>4</sub>).

| Polymorph                                        | 1a           | 1b (Cu1)     | 1b (Cu2)     | 1c           |
|--------------------------------------------------|--------------|--------------|--------------|--------------|
| $\theta_x$ (°)                                   | 83.5         | 87.5         | 87.5         | 79.3         |
| $\theta_y$ (°)                                   | 86.1         | 80.3         | 88.9         | 88.0         |
| $\theta_z$ (°)                                   | 81.5         | 88.8         | 88.8         | 88.1         |
| $\tau_4$ <sup>1</sup>                            | 0.725        | 0.715        | 0.742        | 0.708        |
| $\tau_4'$ <sup>2</sup>                           | 0.713        | 0.700        | 0.736        | 0.705        |
| $\sigma^2$ (° <sup>2</sup> ) <sup>3</sup>        | 521.7        | 481.9        | 470.2        | 477.3        |
| Mean distance (Cu-N) (Å)                         | 2.008(2)     | 2.022(2)     | 2.029(2)     | 2.019(1)     |
| $\zeta$ (Å) <sup>4</sup>                         | 0.0391       | 0.0044       | 0.0394       | 0.0568       |
| D (Å) <sup>5</sup>                               | 0.0049       | 0.0055       | 0.0048       | 0.0070       |
| dmp-dmp l.s.p. angle (°) <sup>6</sup>            | 79.19        | 88.25        | 90.00        | 88.27        |
| Cu displacement from dmp l.s.p. (Å) <sup>6</sup> | 0.265, 0.008 | 0.113, 0.036 | 0.047, 0.118 | 0.000, 0.181 |

<sup>1</sup> Tau 4 tetrahedral distortion parameter [41]. <sup>2</sup> Tau 4' tetrahedral distortion parameter [42]. <sup>3</sup> Bond angle variance [43].  $\sigma^2 = \frac{1}{n-1} \sum_{i=1}^n (\phi_i - \phi_0)^2$ . <sup>4</sup> length distortion [44].  $\zeta = \sum_{i=1}^n (l_i - l_{av})$ . <sup>5</sup> Baur's length distortion index [45].  $D = \frac{1}{n} \sum_{i=1}^n \frac{|(l_i - l_{av})|}{l_{av}}$ . <sup>6</sup> least-squares planes formed by only aromatic C and N atoms of dmp ligands.

Distortion angles  $\theta_x$ ,  $\theta_y$ , and  $\theta_z$  were calculated as defined by the method of White [46] and further employed by Coppens [26]. Rocking distortions are measured using  $\theta_x$  and  $\theta_y$ . Rocking distortions measure changes between nearly tetrahedral geometry to more trigonal pyramidal geometry. The angle  $\theta_z$  is a measure of flattening distortion. Idealized tetrahedral geometry using these distortion metrics yields values of  $\theta_x = \theta_y = \theta_z = 90^\circ$ . A trigonal pyramidal geometry has distortion values  $\theta_x = \theta_y = 0^\circ$  and  $\theta_z = 90^\circ$ . A square planar geometry has  $\theta_x = \theta_y = 90^\circ$  and  $\theta_z = 0^\circ$ . The twisting measure used employs measures of the angle between least-squares planes calculated using all non-hydrogen atoms of each dmp with the exception of the methyl groups as these are seen to deviate from the dmp plane in several instances. An idealized tetrahedral geometry has a twisting value of  $90^\circ$ , whereas the opposite extreme of square planar geometry has a twisting angle of  $0^\circ$ . Twisting also implies flattening of the coordination sphere so this measure incorporates some information from the purer flattening distortion angle  $\theta_z$  as well.

Additional quantitative coordination environment angular distortion measures for **1a**, **1b**, and **1c** are summarized in Table 2. Both  $\tau_4$  and  $\tau_4'$  [47], measures of tetrahedral distortion, for each unique copper coordination environment are reported. The  $\tau_4$  and  $\tau_4'$  parameters have idealized values of 1 for purely tetrahedral geometry, 0 for an idealized square planar geometry, and 0.43 and 0.34 (respectively) for a pure see-saw distorted geometry. As the bidentate dmp bite angle is restrained by bonding to the Cu(I) center (N-Cu-N bite angle average =  $82.5^\circ$ , max =  $83.1^\circ$ , min =  $81.6^\circ$ ), and the largest valence angles at Cu are employed, these bis-bidentate systems cannot achieve terminal  $\tau$  values of 1 for tetrahedral coordination. The bond angle variance  $\sigma^2$  is also reported [47]. This measure of distortion, while less specific than other measures of distortion, provides an absolute magnitude of total angle deviation from idealized tetrahedral geometry. The idealized tetrahedral geometry has a bond angle variance of zero. As the coordination of dmp to the copper(I) ion forming the 5-membered chelate ring enforces typical bite angles of  $80$ – $83^\circ$ , the bond angle variance is therefore significantly skewed from a small bond angle variance.

Close inspection reveals intriguing distortion patterns within these polymorphs. Given the  $\theta_x$  and  $\theta_y$  values, **1c** demonstrates the largest rocking distortion in one dmp ( $\theta_x = 79.3^\circ$ ). The two unique molecules of the asymmetric unit in **1b** have one large distortion in the Cu1 ( $\theta_y = 80.3^\circ$ ) while the other molecule (Cu2) is much less distorted ( $\theta_y = 88.9^\circ$ ). The more distorted Cu1 of **1b** and **1c** are quite similar. Polymorph **1a** has intermediate distortions distributed both in  $\theta_x$  and  $\theta_y$  ( $83.5^\circ$ ,  $86.1^\circ$ , respectively). **1a** also has the largest flattening

distortion as measured by  $\theta_z$  ( $81.5^\circ$ ), while the other  $\theta_z$  values are nearly constant across these polymorphs. Polymorph **1a** also shows the largest twisting distortion ( $79.19^\circ$ ) from the idealized  $90^\circ$  between dmp least-squares planes, while the three other unique copper centers show twisting between  $88$ – $90^\circ$  that confirm the asymmetry of Cu1 and Cu2 coordination geometries in **1b** (larger  $\tau$  values for Cu2). Similar  $\tau^4$  and  $\tau^{4'}$  distortion magnitudes for each copper coordination in the range of  $0.700$ – $0.742$  place each coordination geometry squarely in the range of highly distorted tetrahedral geometry in the direction of a see-saw geometry. The bond angle variance also highlights the largest tetrahedral angle distortions in **1a** ( $521.7^\circ$ ) vs. more similar values for the other polymorph copper geometries.

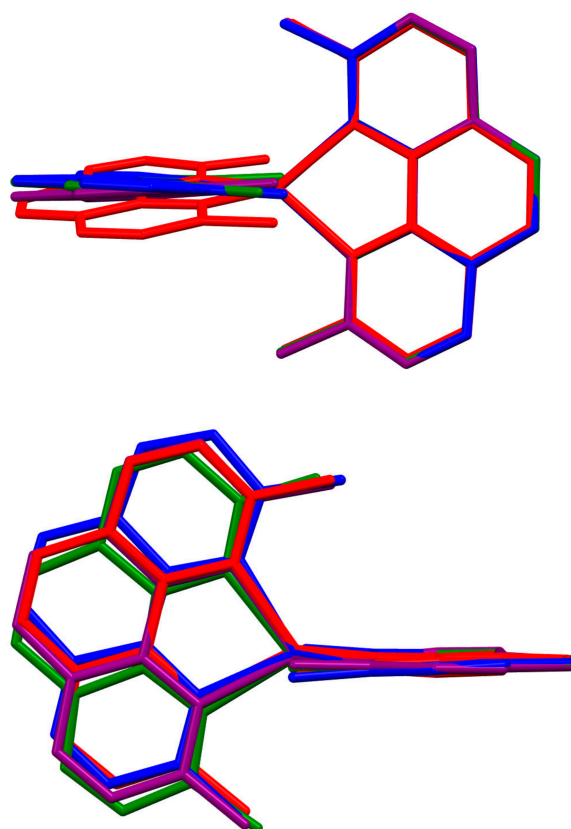
Additional distortions based on bond lengths and angles were also calculated, including the mean Cu-N bond distance, Baur's distance distortion index (D) [47], Cu-N bond length distortion ( $\zeta$ ) [47], and the displacement of Cu from the dmp least-squares planes [48]. Baur's distortion index is equal to zero when all bond lengths are equal, with increasing D values indicating greater distortions. The mean Cu-N distances of **1a** are statistically significantly shorter than those of **1b** and **1c**. However, comparison of the bond length distortion parameter  $\zeta$  (a measure of deviation from the average Cu-N bond length) indicates **1b**(Cu1) has the smallest value, much larger and similar values for **1a** and **1b**(Cu2), and the largest value for **1c**. Baur's distortion index indicates the largest bond length differences for **1c** while **1a** and **1b**(Cu2) have the smallest bond length deviations. The displacement of Cu out of the dmp least-squares plane in all cases demonstrates favoring a dissymmetry favoring Cu towards more planarity with one dmp. The largest difference in values between the two Cu displacements is observed in **1a**.

An overlay of the  $[\text{Cu}(\text{dmp})_2]^+$  cation coordinates of each unique cation in the three polymorphs is shown in Figure 2 [48]. Table 3 summarizes the root-mean-squared difference in the atom coordinates of each unique copper cation (excluding hydrogen atoms). While the r.m.s. deviation of the structural coordinates of two species is a more rudimentary measure of similarity between the intramolecular features of the  $[\text{Cu}(\text{dmp})_2]^+$  cations in the polymorphs, the same trends are observed within this series as the more specific metrics described earlier. The cation of **1a** has both the largest absolute overall coordinate r.m.s. deviation and max atom...atom coordinate deviations from the best overlap fit in this series of polymorphs. The large cation coordinate overlay deviations for **1a** compared with the cations of **1b** and **1c** are consistent with significant differences in other intramolecular metrics including **1a** having the largest bond angle variance in this series, the largest angle between dmp-dmp least-squares planes, and the largest value of Cu displacement from the dmp least-squares plane in this series. Though the cation coordinates of **1a** have a larger r.m.s. deviation of coordinates with all the other cations of **1b** and **1c** than other comparisons, the magnitude of the deviation does not exceed the  $>0.375$  Å difference suggested by Bernstein [17] to meet the classification as conformational polymorphs.

**Table 3.** Root-mean-squared difference in the non-H atom coordinates and maximum deviations of pairwise atom coordinates of  $[\text{Cu}(\text{dmp})_2]^+$  cations in polymorphs **1a**, **1b**, and **1c**<sup>1</sup>.

| Polymorph Cation Pair            | r.m.s. Deviation (Å) | Max Deviation (Å) |
|----------------------------------|----------------------|-------------------|
| <b>1a/1b</b>                     | 0.2672               | 0.5298            |
| <b>1a/1c</b> (Cu2)               | 0.2411               | 0.4949            |
| <b>1a/1c</b> (Cu1)               | 0.2643               | 0.5041            |
| <b>1b/1c</b> (Cu1)               | 0.1296               | 0.2840            |
| <b>1b/1c</b> (Cu2)               | 0.1428               | 0.2617            |
| <b>1c</b> (Cu1)/ <b>1c</b> (Cu2) | 0.1156               | 0.2788            |

<sup>1</sup> Hydrogens and  $\text{BF}_4^-$  anions excluded from the r.m.s calculations.



**Figure 2.** Overlap of the  $[\text{Cu}(\text{dmp})_2]^+$  cation coordinates of each unique cation in the polymorphs **1a**, **1b**, and **1c**. Above, view perpendicular to the best overlap fit of one dmp ligand in each unique  $[\text{Cu}(\text{dmp})_2]^+$  cation. Below, view parallel to the best overlap fit of one dmp ligand in each unique  $[\text{Cu}(\text{dmp})_2]^+$  cation. Red **1a**, blue **1b**, purple **1c** (Cu1), green **1c** (Cu2).

### 3.3. Intermolecular Packing Comparison of Polymorphs

A common intermolecular feature found in most structures of  $[\text{Cu}(\text{dmp})_2]^+$  involves  $\pi$ -stacking of the dmp ligands [26,27]. As  $\pi$ -stacking can strongly modify emission wavelength and quantum yield through the extent and geometric nature of the  $\pi$ -overlap or possible excimer formation, examination of these differences may give insights into possible photoluminescence differences between these polymorphs. Metrics describing the  $\pi$ - $\pi$  interactions of each polymorph are found in Table 4.

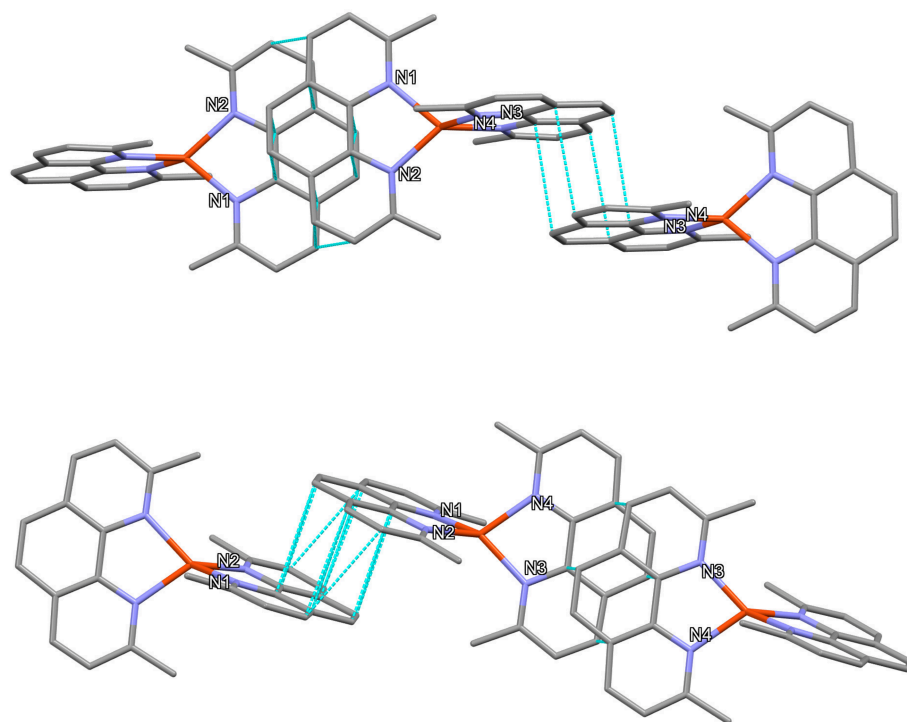
**Table 4.**  $\pi$ - $\pi$  stacking comparison of three polymorphs of  $[\text{Cu}(\text{dmp})_2](\text{BF}_4)$ .

| Polymorph                                       | 1a           | 1b (Cu1)     | 1b(Cu2) | 1c    |
|-------------------------------------------------|--------------|--------------|---------|-------|
| Stacking pattern                                | homo-dimeric | homo-dimeric | none    | none  |
| Stacking distance(s) <sup>1</sup> (Å)           | 3.365, 3.429 | 3.288        | NA      | NA    |
| $\pi$ stacking slippage <sup>2</sup>            | 3.824, 4.235 | 6.41         | NA      | NA    |
| Shortest intermolecular Cu...Cu distance(s) (Å) | 8.626, 8.947 | 8.893        | 7.063   | 7.115 |

<sup>1</sup> Calculated distance between least-squares planes formed only by aromatic carbon atoms and nitrogen atoms of each dmp ligand. <sup>2</sup> Calculated distance between centroids formed only by aromatic carbon atoms and nitrogen atoms of each dmp ligand.

Three different patterns of  $\pi$ -stacking are observed in this series of three polymorphs. Polymorph **1c** packs with no evidence of parallel offset face-to-face  $\pi$ -stacking (Figure S1). Polymorph **1b**, with  $Z' = 2$ , shows nominal homo-dimeric parallel offset face-to-face  $\pi$ -stacking between symmetry-related dmp ligands of the Cu1 cations, while the Cu2

cations do not show any  $\pi$ -stacking interactions (Figure S2). The Cu1 dmp...Cu1 dmp  $\pi$ -overlap is minimal with a slipped dmp centroid...dmp centroid distance of 6.41 Å. However, polymorph **1a** engages in extensive  $\pi$ -stacking with each of the unique dmp ligands (Figure 3). Polymorph **1a** packs in two unique homo-dimeric parallel offset face-to-face  $\pi$ -stacking interactions between symmetry-related dmp ligands of the cations. So, each cation in **1a** engages in two different  $\pi$ -interactions, one of each type of  $\pi$ -overlap with symmetry related cations.

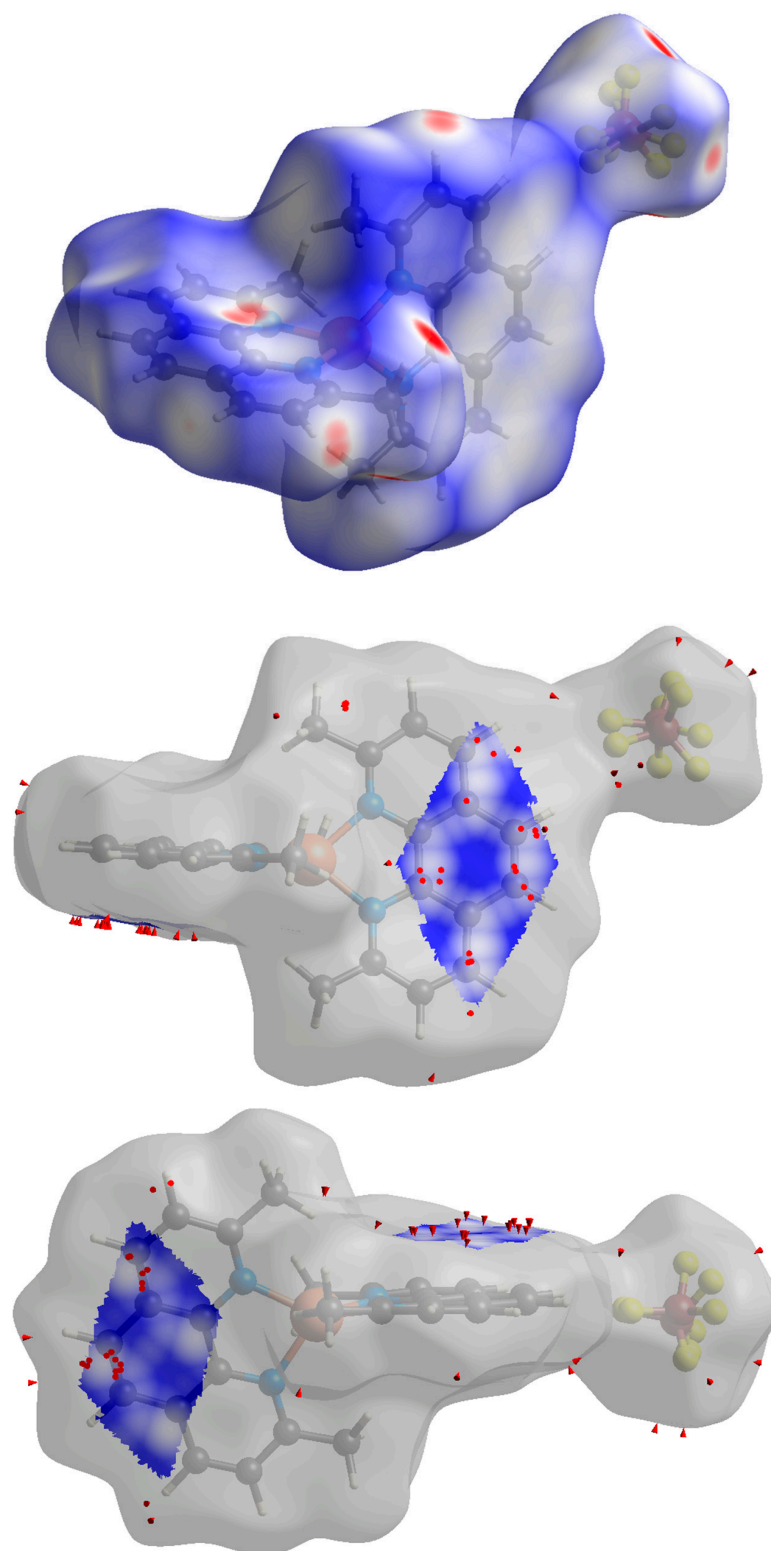


**Figure 3.**  $\pi$ -stacking motif in the structure of **1a**. Above, view is perpendicular to the N1, N2, C2–C13 least-squares planes. Below, view is perpendicular to the N3, N4, C16–C27 least-squares planes. Dotted blue lines indicated C...C atom contacts less than the van der Waals radii sums.  $\text{BF}_4^-$  anions and hydrogen atoms omitted for clarity. Carbon atoms gray, nitrogen atoms blue, copper atoms orange.

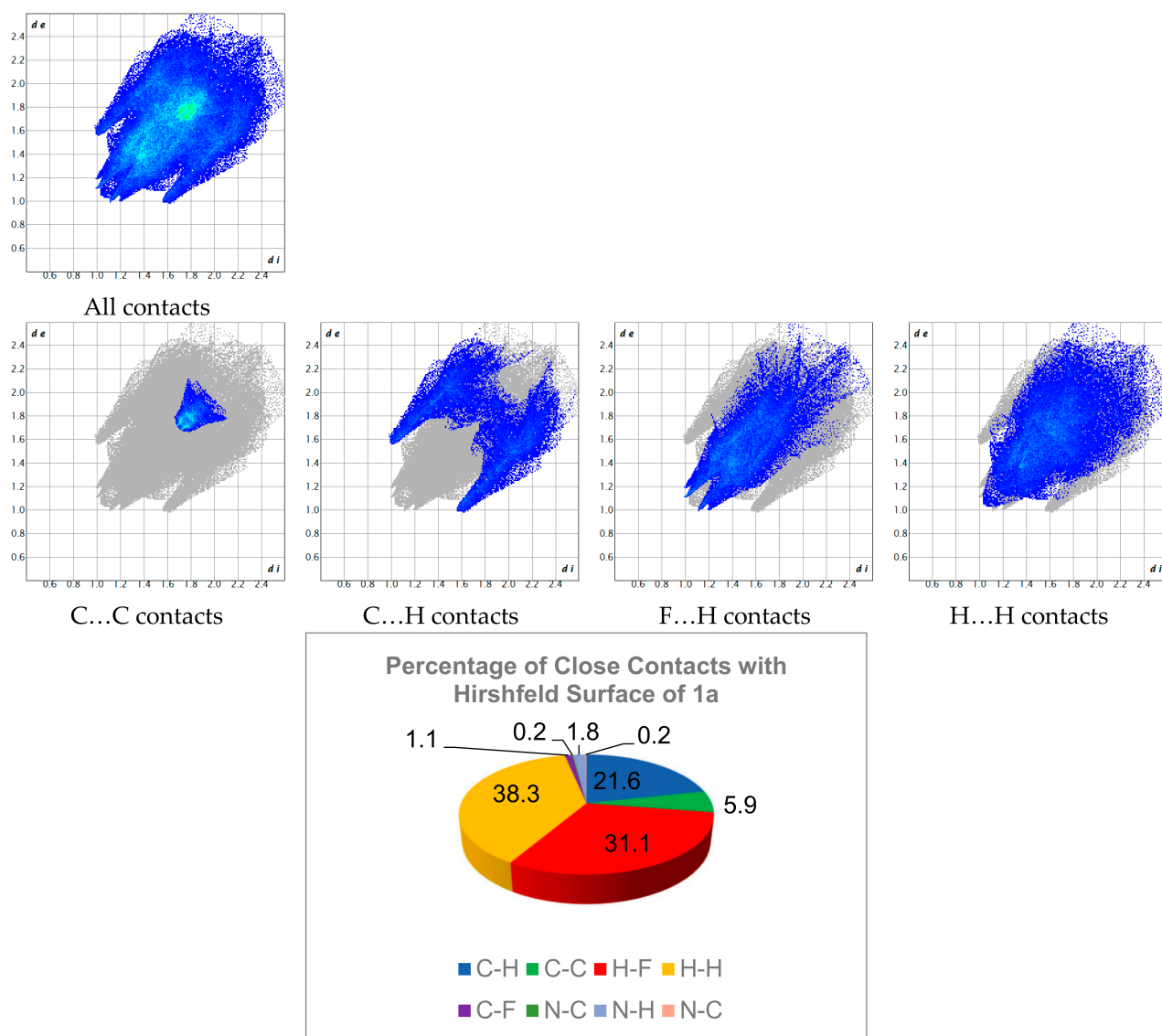
Intermolecular contacts reveal trends in these polymorphs that indicate interactions beyond face-to-face  $\pi$ -stacking. Tables S3, S4, and S5 summarize short contacts less than van der Waals radii sums for each of the polymorphs **1a**, **1b**, and **1c**, respectively. The shortest intermolecular atom...atom contacts in all polymorphs are dominated by H...F and C...H contacts. In **1a**, six unique C...H contacts are dmp aromatic C-H...dmp aromatic C edge-to-face interactions. With extensive  $\pi$ -stacking observed in **1a**, nine aromatic C...aromatic C contacts are also present. On the other hand, **1c** with less  $\pi$ -stacking has only four aromatic C...aromatic C contacts and a single dmp C-H...dmp aromatic C edge-to-face interaction is present. Polymorph **1b** exhibits no  $\pi$ -stacking, zero aromatic C...aromatic C contacts, and zero dmp aromatic C-H...dmp aromatic C edge-to-face interactions.

Hirshfeld surfaces calculated for each polymorph allow visualization of these close contacts (Figure 4 (**1a**), Figure S3 (**1b**), and Figure S4 (**1c**)) [49]. Fingerprint plots and a breakdown of the percentage of close contacts calculated from the Hirshfeld surface are shown in Figure 5 (**1a**), Figure S5 (**1b**) and Figure S6 (**1c**). The red areas on the Hirshfeld surface in Figure 4 (upper) demonstrate the shortest intermolecular contacts with neighboring groups. A closer inspection of only the C...C contacts with all contacts mapped

onto the surface (Figure 4 middle, lower) demonstrate a concentration of intermolecular interactions on the face of the dmp ligands, consistent with  $\pi$ -stacking.



**Figure 4.** Hirshfeld surfaces of polymorph **1a**. Upper, complete Hirshfeld surface with plotted  $d_{\text{norm}}$  range  $-0.25$  to  $1.25$ . Middle, Hirshfeld surface with only C...C contacts area highlighted in blue, plotted  $d_{\text{norm}}$  range  $0$  to  $0.25$ . Red cones indicate all contact locations on the Hirshfeld surface where  $d_i = d_e = 1.8$ . Lower, view perpendicular to middle view.



**Figure 5.** Fingerprint plots from the Hirshfeld surface of **1a** and percentages of each specific type of close contact.

In each polymorph, the three largest contributors to short contacts with the Hirshfeld surface are H...H, H...F, and C...H contacts (90% or greater in combination for **1a**, **1b**, and **1c**). The vast majority of C-H contacts are in each case aromatic C-H (not methyl group C-H). In each polymorph Hirshfeld surface, aromatic C-H and F contacts with neighbors are most apparent. Close inspection of **1a** shows a short contact in the face of the  $\pi$ -system of each dmp ligand. This is present where a  $\pi$ -stacked neighbor encounters each dmp ligand. The enhanced  $\pi$ -stacking of **1a** relative to **1c** and **1b** is also consistent with the percentage of close C...C contacts in the Hirshfeld analysis (**1a** = 5.9%, **1c** = 2.0%, **1b** = 1.5%). The percentage of short C...H contacts concomitantly decreases across the same series (**1a** = 21.6%, **1c** = 25.6%, **1b** = 31.1%) consistent with less  $\pi$ -stacking. Across the polymorph series, H...H contacts remain relatively constant.

The density of the structures follows the trend where structure **1a** engages in the most  $\pi$ -stacking and has the greatest density, **1b** with some  $\pi$ -stacking has intermediate density, and **1c** with no  $\pi$ -stacking has the lowest density. This trend is in opposition to the typical expected positive thermal expansion associated with higher data collection temperatures if no polymorphic transition occurred. Using a mean volumetric thermal expansion coefficient ( $161 \times 10^6 \text{ K}^{-1}$ ) [50], the unit cell volume at 293 K for **1a**, and a

decrease of 203 K from 293 K to 90 K, if **1a** were cooled and did not undergo a phase change, the expected density at 90 K would be 1.574 g/cm<sup>3</sup>.

#### 4. Conclusions

The new third polymorph **1a** reported here shows significant differences in both intra- and intermolecular features compared with the previously reported polymorphs **1b** and **1c**. Amongst the three polymorphs compared for [Cu(dmp)<sub>2</sub>](BF<sub>4</sub>), polymorph **1a** has the largest intramolecular dmp...dmp l.s.p. angle, the largest copper coordination sphere bond angle variance, shortest mean Cu-N distances, and the largest r.m.s. difference in the non-H atom coordinates compared with each unique [Cu(dmp)<sub>2</sub>]<sup>+</sup> in this series. Polymorph **1a** exhibits the largest proportion of C...C contacts as determined by Hirshfeld surfaces, shows unique  $\pi$ -stacking interactions with each dmp ligand, and has the highest density of these three polymorphs. While changes in anion or solvate formation may lead to larger changes in intra- and intermolecular interactions, discovery of **1a** suggests even different solvents used in crystallization, all crystallized at the same temperature, can modify polymorph formation, even with a relatively rigid bidentate cation such as [Cu(dmp)<sub>2</sub>]<sup>+</sup>.

Future studies to characterize the mechanochemically derived [Cu(dmp)<sub>2</sub>](BF<sub>4</sub>) reaction product to evaluate possible mixtures of polymorphs produced compared with solution reaction derived solids are underway.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/cryst16080492/s1>, Table S1: Crystal data and structure refinement for **1a**, Table S2: Crystallographic data comparison of three polymorphs of [Cu(dmp)<sub>2</sub>](ClO<sub>4</sub>), Table S3: Short intermolecular contacts of polymorphs **1a**, Table S4: Short intermolecular contacts of polymorphs **1b**, Table S5: Short intermolecular contacts of polymorphs **1c**, Figure S1: Packing diagram of **1c** showing no  $\pi$ -stacking is present in this structure, Figure S2: Homo-dimeric  $\pi$ -stacking of dmp groups on Cu1 of **1b**, Figure S3: Hirshfeld Surface of **1b**—plotted  $d_{\text{norm}}$  range −0.25 to 1.25, Figure S4: Hirshfeld Surface of **1c**—plotted  $d_{\text{norm}}$  range −0.25 to 1.25, Figure S5: Fingerprint plots from the Hirshfeld surface of **1b** and percentages of each specific type of close contact, Figure S6: Fingerprint plots from the Hirshfeld surface of **1c** and percentages of each specific type of close contact. CIF check for **1a**.

**Author Contributions:** Conceptualization, methodology, formal analysis, writing—original draft preparation, visualization, project administration, D.E.J. Funding acquisition, writing—review and editing, synthesis and crystallization, investigation, K.O. and D.E.J. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Summer Scholars Undergraduate Research Program, St. Catherine University. The X-ray diffractometer was funded through the NSF-MRI grant # 1125975 ‘MRI Consortium Acquisition of a Single Crystal X-ray Diffractometer for a Regional PUI Molecular Structure Facility’.

**Data Availability Statement:** CCDC 2571612 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**Conflicts of Interest:** The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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