



# Article Overlooked Solid State Structure of 1,3-I<sub>2</sub>C<sub>6</sub>F<sub>4</sub>—The *Meta*-Member of an Iconic Halogen Bond Donors Trio

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**Abstract:** The solid-state structure of the *meta*-isomer of diiodotetrafluorobenzene (DITFB), the sole liquid DITFB at 25 °C, is reported. Computational and comparative analyses of its crystal packing have elucidated potential factors contributing to its lower melting point and reduced affinity as a halogen bond donor conformer as compared to the *para*-isomer. This discussion also addresses the lower melting points of *ortho*- and *meta*-isomers in general. The platelet crystal habit of 1,3-DITFB is examined in relation to its energy framework pattern, proposing a comprehensive and illustrative predictive model for its faster growth in the [001] direction. This growth aligns with the maximum attachment energy.

**Keywords:** halogen bonding; Carnelley's rule; isomers; melting point; DITFB; diiodotetrafluorobenzene;  $C_6F_4I_2$ ; energy frameworks; Crystal Explorer; crystal habit; morphology

# 1. Introduction

The ongoing progress in the study of halogen bonding [1-3] and its positive impact on crystal engineering [4,5], is inseparably linked with diiodotetrafluorobenzenes (DITFB). In contrast to diiodoacetylene, which is easily oxidized, potentially explosive, or light-sensitive perfluorinated iodoalkanes, the DITFBs remain the preferred choice as halogen bond (XB) donors [6]. They are favored due to their remarkable chemical and thermal stability, inert nature, solubility in organic solvents, highly polarized iodine atoms, and commercial availability [7]. Among these, the trio of ortho-, meta-, and para-diiodotetrafluorobenzenes (DITFB) has contributed to approximately 820 co-crystal structures deposited in the CSD by the end of 2022. While this number continues to grow annually for all three isomers, it is worth noting that the proportion of co-crystals formed by ortho- and meta-DITFBs is roughly an order of magnitude lower than that of para-DITFB. These values may not precisely reflect the propensity of DITFB isomers to form co-crystals, as not all three isomers were consistently utilized in every series of co-crystallization experiments. Nevertheless, considering their nearly equal commercial availability, our own experiences and literature data, we can assume that this distribution provides a reliable indication of their relative capacity to engage in co-crystal formation.

A similar disparity as mentioned above for the number of co-crystals deposited in the CSD, is also apparent in the physical properties of the *o*-, *m*-, and *p*-DITFB isomers. The *p*-DITFB, which exhibits the highest melting point (107–108 °C) and is the most symmetrical, contrasts with the *meta*-DITFB, which has a lower melting point (23–26 °C), and the ortho-DITFB, which falls in between 49–50 °C.

With this observation in mind, we studied the correlation between a specific coformer's ability to form co-crystals and its physical properties related to intermolecular interactions, such as solubility, melting point, and enthalpy of sublimation.

The comparison of packing patterns between coformers in their native crystals and their respective co-crystals has become a routine aspect of our co-crystal structure analysis.



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). It is noteworthy that this similarity is observed quite often, so that the crystal packing in the parent crystal closely resembles that in its co-crystal. The absence of such similarity is in turn intriguing and suggests further investigation. For certain co-formers, we have observed stable modular architectures in a series of their co-crystals that differ from the typical structures found in their native crystals. The diiodotetrafluorobenzenes (DITFBs) are again an exemplary case. While these compounds form van der Waals (vdW) native crystals with a herringbone close packing arrangement, they reconfigure into columnar or dimeric stacked aggregates in XB-assisted co-crystals. It is important to note that this is true for 1,4- and 1,2-DITFB, but only partially for 1,3-DIFTB, as its native crystal structure has not yet been investigated.

Given the significance of DITFBs in crystal design, this oversight appears challenging in the course of our ongoing XB-assisted crystal engineering research. The fact that 1,3-DITFB is liquid at standard room temperature (melting around 23–26 °C) is not a significant issue in modern crystallography techniques. However, it raises an important question of the lower melting points observed in *meta*-isomers compared to *para*- and *ortho*isomers [8–10]. The common answer given is Carnelley's rule [11] but the most critical and still actual review on this topic by Gavezzotti admits that "*Two blobs aligned with the center of the phenyl ring are better suited for packing than two blobs along directions forming a* 120° *or 60° angle at the center of the phenyl ring. How and why this observation is related to the various contributions of the intermolecular forces involved, and to their consequences on crystal structure adoption, is a question that still awaits an answer*" [8]. Therefore, in this study, we present the crystal structure of 1,3-DITFB and address the issue of lower melting points observed in *meta*-isomers. While this work does not provide a comprehensive solution, it may pave the road to solve this apparently straightforward question.

#### 2. Materials and Methods

Solvents were purified, dried and distilled in an argon atmosphere before use. Commercial 1,3-DITFB was used without additional purification.

## 2.1. Crystallization of 1,3-DITFB

A drop of a saturated solution of 1,3-DITFB in heptane was placed on a microscope glass slide and allowed to evaporate at ambient temperature (17 °C) to produce color-less significantly twinned plates of poor quality. The same solution was kept at -10 °C overnight, yielding similar colorless plate-like crystals. The resulting crystals are too large for single-crystal XRD analysis, and all attempts to mechanically separate fragments of suitable size resulted in a significant quality loss, likely due to plasticity noticeable down to -25 °C. Further cooling with evaporating liquid nitrogen flow resulted in crystal cracking. Therefore, the oversized crystals grown from heptane were used for face-indexing only (T = 290 K).

A sample for crystal structure determination was prepared in a 150  $\mu$ m mylar capillary filled with liquid 1,3-DITFB and sealed with epoxy resin. Specifically, the capillary was glued with epoxy resin into the metal tube of the appropriate length and diameter (metal tube was cut from the syringe needle) and sealed at the same time. It was filled with the liquid 1,3-DITFB by placing the open end of a sealed capillary into the 1,3-DITFB inside the Schlenk tube, which was then vacuumed to allow the liquid to fill the tube. The Schlenk tube was slowly filled with air, capillary was gently removed from the Schlenk tube and its open end was sealed with another drop of epoxy resin. This assembly was fixed inside the metal tube of the standard XRD goniometer head mount (Figure A1, see Appendix A).

The goniometer head with the capillary was mounted and centered in a 294 K stream of nitrogen (Oxford Cryosystems, Hanborough, UK). The temperature T = 294 K was chosen as it was only ~4 K below the melting point of 1,3-DITFB, which is 298 K. A single crystal readily formed in the middle of the tube exposed to the stream of cold nitrogen within 5 min. Subsequently, the system was cooled down to 290 K at a rate of 30 K per hour, at which all the data were collected.

## 2.2. Computational Details

## 2.2.1. Intermolecular Interactions and Lattice Energy

Intermolecular interaction energy calculation and subsequent lattice energy calculations and energy frameworks generation for 1,3-DITFB were performed using experimental crystal geometry in Crystal Explorer 21.5 (TONTO 18.10.24, CE-B3LYP/DGDZVP) [11] for all unique molecular pairs in the 20 Å cluster around the central molecule. Further details on the energy frameworks and lattice energy calculations in Crystal Explorer 21.5 are available at the program web-site (https://crystalexplorer.net/docs/category/energies, accessed on 10 July 2023).

## 2.2.2. MEP

Theoretical calculations were carried out with the ORCA 5.03 program package [12]. A non-hybrid PBE functional [13] dispersion correction with Becke–Johnson damping (D3BJ) [14,15] and a def2-TZVP basis set [16] with small-core pseudopotential for I atoms [17] were used for geometry optimization. Def2/J auxiliary basis [18] was used for Coulomb fitting. Electron density calculations of the resulting geometries were performed using ZORA approximation for scalar relativistic effects [19,20], a hybrid functional PBE0 [21]. An all-electron def2-TZVP basis set recontracted for ZORA was used on light atoms and SARC-ZORA-TZVP basis set was used on iodine [22]. RIJCOSX approximation [23] in combination with a SARC/J auxiliary basis set [24] was used to improve computational speed. MEP values on 0.001 eÅ<sup>-3</sup> isosurfaces were evaluated by the Multiwfn program [25]. MEP figures were prepared using VisMap software 4.2 [26].

## 2.3. Single Crystal X-ray Crystallography

A Bruker APEX II CCD area detector diffractometer, equipped with a low-temperature attachment (Oxford Cryosystems), was used for the cell determination and intensity data collection. The data were collected using the standard phi–omega scan techniques and were reduced using SAINT v8.37 A (Bruker, 2015). The SADABS (Bruker, 2016) software was used for scaling and absorption correction. Structures were solved by intrinsic phasing method and refined using least squares method for F<sup>2</sup> in anisotropic approximation in SHELXTL and Olex2 software [27,28]. Atomic coordinates and other structural parameters of 1,3-DITFB have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2297695, contains the supplementary crystallographic data for this paper.

## 3. Results and Discussion

## 3.1. Crystal Preparation and Molecular Structure of 1,3-DITFB

The cooling of liquid 1,3-DITFB in a sealed capillary tube to 294 K results in the formation of acicular Pnma crystals suitable for SC-XRD analysis. The molecular geometry of 1,3-DITFB, as revealed from this native crystal structure solution, is expectedly identical to that in its co-crystals (Figure A2, see Appendix A).

Iodine atoms in the 1,3-DITFB molecule form intermolecular halogen bonds (XBs) in the solid-state structure (Figure A3 in Appendix A). Each iodine atom acts both as an XB-bond donor (along the extension of the C-I bond) and an XB-acceptor in the region of its p-belt [14]. The I···I contacts measure 4.016(2) Å (Figure 1b). These distances are shorter than the sum of the revised van der Waals (vdW) radii for iodine ( $2 \times 2.17$  Å [29]), lie on the edge of the vdW radii revised by Alvarez ( $2 \times 2.04$  Å [30]), and even exceed the sum of the classic Bondi's vdW radii ( $2 \times 1.98$  Å [31]). Without delving deeply into the debate on which vdW radii revision is more suitable and applicable in this context, it is evident that this I···I distance indicates a relatively weak XB. This assessment finds support in the intermolecular interaction energy computations (-7 kJ/mol, CE-B3LYP/DGDZVP, Figure A3). Simultaneously, the  $\angle$ C-I···I angles surrounding this XBs are close enough to 90° and 180° ( $\angle$ C(1)-I(1)···I(2) 158.3(3)°,  $\angle$ C(3)-I(2)···I(1) 106.8(3)°, Figure 1b) to indicate that despite its weakness, this XB is indeed a genuine one, (type-II XB, [32,33]).



**Figure 1.** (a) Fragment of the crystal packing of 1,3-DITFB, showing the I···I XB interactions geometry (I(1) ··I(1) 4.016(2)Å (normalized to iodine vdwW radii sum [29]: -0.07465),  $\angle C(1)$ -I(1)···I(2) 158.3(3)°,  $\angle C(3)$ -I(2)···I(1) 106.8(3)°,  $\angle C(1)$ -I(1)···I(2a) 106.8(3)°,  $\angle C(3a)$ -I(2a)···I(1) 158.3(3)°), and (b) their total intermolecular interaction energy (kJ/mol, red dashed lines: I···F contacts, green: F···C; violet: I–I).

Although these I···I type-II XB interactions are the most subjectively interesting interactions present in this crystal, they are not the strongest interactions in the solid 1,3-DITFB. The energy of intermolecular interaction in these I···I halogen-bonded associates is only -7 kJ/mol, compared to -20 and -24 kJ/mol for the intermolecular interactions that are stabilized by multiple predominantly dispersive C-F···C and C-F···I contacts (Figures A3–A8, Tables A1–A3). The herringbone packing pattern of 1,3-DITFB (Figure A3b) is indicative of a mere close packed arrangement that is not influenced by strong specific intermolecular interactions. It is commonly found in compact, planar molecules such as unfunctionalized polycyclic aromatic hydrocarbons like naphthalene, anthracene, phenanthrene, etc., [34]. Owing to the far lower specificity and directionality of these F···C and F···I interactions, we can hardly discuss them in terms of reliable supramolecular synthons. However, one can see (Figure A7) that the total energy of intermolecular interaction correlates with the number of short interactionic I···F and C···F contacts in a given pair of molecules.

The packing patterns observed in 1,3-DITFB (*Pnma*) are largely defined by close packing rather than specific directional intermolecular interactions. These can be represented as I···I stabilized layers (Figure A3a, see Appendix A), C···F/I···F stabilized chains, stacks, etc., depending on the subjective understanding of the importance of certain interatomic interactions. Even the very concept of interatomic interactions as the factor that defines crystal structure can be questioned from a purely thermodynamic pole [35–38]. Therefore, in further discussion, we analyze the intermolecular interaction energies and their frameworks in the solid state of 1,3-DITFB and its co-crystals, which is a middle path and allows balanced understanding of a crystal packing.

### 3.2. Intermolecular Interactions Energy in the XB-Assisted Co-Crystals of 1,3-DITFB

Analyzing the co-crystal structures in parallel with the respective structures of their parent crystals (co-formers) provides a broader perspective on crystal structures. From this perspective, they are not seen as standalone entities but as integral components of a general crystallization landscape [6,39–43]. Considering the molecular level of interactions in the co-crystals, or in other words, only pairwise interactions between the XB-donor and XB-acceptor molecular members of a short-range supramolecular synthon is not sufficient for understanding co-crystal stabilization. Detailed comparison of isomeric

*meta-* and *para-*diiodotetrafluorobenzene as XB-donors in crystal engineering by Bedekovi et al. also emphasizes the similarity of local XB (I···N) geometry versus different efficiency of crystal packing upon switching from a linear halogen bond donor 1,4-DITFB to the bent 1,3-DITFB [7]. From an energetic point of view, it is worth noting that, despite actual differences in their propensity to form co-crystals, the  $V_{max}$  of ESP in *o-*, *m-* and *p-*DITFBs are quite close (+29.7 kcal/mol, +30.5 kcal/mol and +31.3 kcal/mol, respectively, Figure 2) and therefore pairwise energies of intermolecular interactions between 1,3-DITFB or 1,4-DITFB with respective XB-acceptors are also close in most of the co-crystals they form.



**Figure 2.** Molecular electrostatic potential (ESP) isosurface maps plotted at 0.001 a.u., with annotated  $V_{\text{max}}$  values (kcal/mol) for (a) 1,2-DITFB, (b) 1,3-DITFB and (c) 1,4-DITFB. Please note that the  $V_{\text{max}}$  values calculated in this study (PBE0/ZORA-def2-TZVP//PBE D3(BJ)/def2-TZVP) are quite close to and follow the same trend as those reported earlier for 1,3-DITFB (+30.76 kcal/mol, PBE0-D3/def2-TZVP [44]) and 1,4-DITFB (+32.6 kcal/mol, PBE0-D3(BJ)/def2-TZVP [45]).

For instance, the total energies of intermolecular interactions (experimental geometry, CE-B3LYP/DGDZVP) of the C=O  $\sigma$ -hole acceptor 2-pyridone [2] with 1,4-DITFB (Figure 3a) are -24.6/-24.2 kJ/mol and almost match those for 1,3-DITFB (-24.3/-27.2 kJ/mol, Figure 3b).



**Figure 3.** The trimolecular fragments of the crystal packing of (**a**) 1,3-DITFB 2-pyridone, (**b**) 1,4-DITTB 2-pyridone [2], and respective intermolecular interaction energies (kJ/mol). Calculated in CE-B3LYP/DGDZVP model [46], dotted lines connect centers of interacting molecules. Note that the intermolecular interaction energy is not exactly the energy of specific interatomic interaction.

Another exemplary pair of 1,3- and 1.4-DITFB co-crystals with 4-cyanopyridine [47] demonstrate not only very close energies of intermolecular interactions (-11.6 kJ/mol

(Figure 4).



Figure 4. The trimolecular fragments of the crystal packing of (a) 1,3-DITFB 4-cyanopyridine, (b) 1,4-DITFB 4-cyanopyridine, and respective intermolecular interaction energies (kJ/mol). Calculated in CE-B3LYP/DGDZVP model [46], dotted lines connect centers of interacting molecules. Note that the intermolecular interaction energy is not exactly the energy of specific interatomic interaction.

However, the close values of intermolecular interactions in their supramolecular synthons are in contrast to the previously mentioned difference in the tendency of 1,3- and 1,4-DITFB to form co-crystals. This underscores that the supramolecular architecture may be determined by lattice efficiency rather than the strength of halogen bonding [7] and indicates the significance of considering the crystal as a whole [48], including the packing symmetry [38,49]. In terms of the supramolecular synthons concept, this means using the long-range supramolecular Aufbau synthon modules (LSAMs [39,50]) rather than mere supramolecular synthons model.

In the case of 1,3-DITFB, its long-range supramolecular modules reveal stacking modules in both its native crystal and the co-crystal with 4-cyanopyridine (Figure 5). Apart from the mere resemblance of these stacks, the XB-acceptor areas, i.e., the lone electron pairs of N atoms of 4-cyanopyridine and the *p*-belts of the I atoms of 1,3-DITFB molecules in the adjacent stack, appear in the same direction, extending from the  $\sigma$ -hole of the iodine atom. This supports the description of I...I contacts in the native 1,3-DITFB as genuine (type-II) halogen bonds (Figure 4).



**Figure 5.** Structural overlay of the 1,3-DITFB stacks in the native crystal (shown in red) and in the cocrystal with 4-cyanopyridine (light-green, nitrogen atoms: blue balls). Iodine atoms are shown as balls. Selected intermolecular distances: I…I 4.016(2)Å, I…N 3.00(1) Å. Notice the similarity of the 1,3-DITFB stacks in both structures and similar positions of XB acceptor atoms (N and I).

The intermolecular interaction energy (which is not exactly the energy of specific interatomic interaction!) in these I···I XB-associated pairs is -6.9 kJ/mol, so it can be categorized as weak XB. These weak I···I XBs are one of the most shortened contacts in 1,3-DITFB crystal (Figure 1a), and seem to form the [51] layered packing pattern (Figure 6a). "Seem" is the keyword here since energy frameworks computations and crystal habit of 1,3-DITFB suggest a totally different vision of packing pattern (Figure 6b).



**Figure 6.** (a) Short contacts layered packing (I–I 4.016(2) Å, dotted lines) vs. (b) the energy frameworks (CE-B3LYP/DGDZVP, blue tubes [46]) layered packing pattern in the native 1,3-DITFB. Both images are displayed in the same [001] views.

### 3.3. Crystal Habit and Energy Frameworks of 1,3-DITFB Native Crystal

The most common approach to understanding the connection between an ideal crystal's inner arrangement and its outer appearance is the Hartman and Perdok Periodic Bond Chain (PBC) theory [52–54]. According to PBC and its subsequent refinements, including the concept of attachment energy [55], it is postulated that the fastest growth occurs in the direction of the crystal face intersected by the greatest number of strong interaction chains. When combined with the energy frameworks concept, which allows the clear visualization of these very "chains of strong interactions", the crystal habit is determined by its energy framework, and clearly observed layers of strong intermolecular interactions may signify the fastest growing direction [56].

The energy frameworks (CE-B3LYP/DGDZVP) for the pair of intermolecular interactions in the native 1,3-DITFB suggest a {010} layered structure for the crystal (Figure 6b). These {010} sheets appear orthogonal to the {001} layered model elucidated from I…I short contacts (Figure 6a). While the I···I XBs are the most chemically meaningful and subjectively interesting elements of the structure here, they exhibit relatively weak interactions (-6.9 kJ/mol) compared to interactions within the {010} layers (-19.7/-23.7 kJ/mol, Figure 7a). Therefore, based on the distinct {010} layered pattern of the energy frameworks of 1,3-DITFB, one can anticipate the formation of platelets with the (010) main face [56] (Figure 6a). However, under sealed capillary cooling crystallization conditions, we observed not plates but pronounced acicular (needle) crystals elongated in the [001] direction (Figure 7b). The [100] direction, which is a component of the {010} plane, partly supports the concept of the most pronounced elements of the energy framework that shape the crystal habit. Nonetheless, the dominance of the [001] direction suggests a closer examination of the interactions within the {010} planes (Figure 7b).



**Figure 7.** (a) The attachment energy for a 1,3-DITFB molecule attaching to the layer (001) face -(13.4 + 13.4 + 19.7) kJ/mol and to (100) face -(13.4 + 23.7) kJ/mol.; (b) face indexing of 1,3-DITFB needle in the capillary tube; (c) face indexing of 1,3-DITFB platelet crystal.

Putting aside the obvious influence of capillary shape, the specific elongation of the crystal in the [001] direction (and not in some other) can be also attributed to the higher attachment energy in this direction -(13.4 + 13.4 + 19.7) kJ/mol, compared to (100) (-(13.4 + 23.7) kJ/mol, Figure 7a).

We can also speculate that [001] direction is in conjunction with the straightforward translational symmetry exhibited by the 1,3-DITFB stacks in the same direction, while zigzag chains in [100] are positioned on a two-fold screw axis. Albeit rather qualitative, this may present evidence of the role of the symmetry factor in stabilizing the crystal lattice [49]. It is important to note the same stacks reappear in the 1,3-DITFB 4-cyanopyridine co- crystal (Figure 5).

After persistent attempts to crystallize 1,3-DITFB, not in a capillary but from a hexane solution cooled in a vial, we finally obtained the expected platelet crystals. Although their quality was not as good as that of the needles from the capillary, their unit cell measurements demonstrated identity with the needle/capillary sample, and their face indexing confirmed the expected (010) main face (see Figure 7c).

## 3.4. Molecular Symmetry and Melting Point

Earlier attempts to rationalize the observed low melting point (m.p.) for 1,3dihalobenzenes [9] suggests the analysis of the geometry of halogen bonding and count of halogen–halogen contacts in the respective packing. Not questioning this approach, but keeping in mind the illustrative analysis of intermolecular interactions energy in chlorinated benzenes, which revealed their columnar structure, in contrast to the layered pattern built upon the short Cl…Cl contacts [57], we compared the crystal energy frameworks and lattice energies of *o*-, *m*-, *p*-DITFB isomers. Since experimental data on  $\Delta H_{subl}$  of DITFBs are absent in the literature and such measurements exceed the scope of this work, we calculated their lattice energies using Crystal Explorer 21.5 (see Materials and Methods Section for computation details). To validate the CE-B3LYP/DGDZVP computational model for DITFBs, we calculated the lattice energy for the series of *para*-dihalobenzenes with the available experimental  $\Delta H_{subl}$  data, and it showed good agreement (Table A5). Calculated lattice energies for *o-*, *m-*, *p*-DITFBs (CE-B3LYP/DGDZVP) appeared rather close, in the range between -85 and -95 kJ/mol (Table 1).

**Table 1.** Lattice energy ( $E_{\text{lattice}}$ , calculated in this work (CE-B3LYP/DGDZVP)) and melting points (literature data) for the isomeric series of DITFBs.

	Elattice	
	kJ/mol	m.p., °C
1,2-DITFB	-96	50
1,3-DITFB	-85	25
1,4-DITFB (α form)	-102	108
1,4-DITFB (β form)	-90	n/a *

\*-the m.p. data in the literature and for commercial samples of *o*- *m*- and *p*-DITFBs (http://fluorine1.ru/search/ formula/C6F4I2, accessed on 29 October 2023; http://www.chemspider.com/Chemical-Structure.61167.html, accessed on 29 October 2023) are available without the reference to the phase composition.

*Meta*-isomer expectedly has a lower lattice stabilization energy (-85 kJ/mol) compared to the others (Table 1). The ~10 kJ/mol difference between the most frequently occurring polymorph of 1,4-DITFB (we called it an  $\alpha$ -form here) and the less frequent one ( $\beta$ -form) is also quite a typical value for the various pairs of polymorphs.

Relatively close values of  $\Delta H_{subl}$  in the series isomers which have strikingly different meting points are not unique for these DITFBs and were earlier noted for an anthracene/phenanthrene pair [58,59]. Common rationalization for the latter is the entropy factor and complex nature of the melting process. As mentioned by Gavezzotti, the melting temperature is just an "unexpensive indicator of crystal cohesion" [8] and their relation is much more complicated than direct, since certain cohesive forces may not be destroyed but remain in the melt.

## 4. Conclusions

In this study, we report the solid-state structure of 1,3-DITFB, an important halogen bond donor co-former, which is liquid at 25 °C. This allows for a comparative analysis of its native crystal packing pattern with those in its co-crystals, which is important for the solution of the primary problem of crystal engineering—understanding of the intermolecular mechanism of the crystal formation. As a first step on this path, we note here the conservation of the stack modular structures found in the native crystal, in its co-crystal with 4-cyanopyridine.

The crystal is stabilized upon C···F, I···F and I···I adhesive intermolecular interactions. The latter are the XBs of type-II and are not the strongest interactions in the crystal by far, which is quite common in XB-assisted crystals and co-crystals. It is particularly important to emphasize this for co-crystals: halogen bonds, chalcogen bonds, and other specific and directed intermolecular interactions that make rational co-crystal engineering possible are not necessarily the strongest interactions in the crystal. However, such not very strong interactions may significantly contribute to the stabilization of the co-crystal lattice, as they may replace interactions (other supramolecular synthons) that are even weaker. Additional stabilization of XB-assisted co-crystals is achieved by adding the energy of XB-donor (say, DITFB) homo-supramolecular modules (usually stacks) to the integral lattice energy of the co-crystal. This means that the analysis of the co-crystal structure should not be limited to pairwise intermolecular interactions, even those that may seem interesting, trendy, chemically meaningful, and important, but should consider the crystal as a whole [38,48,60].

Computational analysis (in Crystal Explorer 21.5 [46]) of the energies of intermolecular interactions in the experimental crystal structure of 1,3-DITFB demonstrate the correlation of the platelet crystal habit with its layered energy frameworks pattern. The calculated attachment energy favors the faster growth of the crystal in the experimentally observed direction. Therefore, the use of Crystal Explorer for the analysis of crystal habit tested here, allows us to suggest it as an unexpensive but reliable method for the assessment of such an external physical parameter of crystal as its habit.

Structural and computational analysis of the correlation between the melting point and molecular symmetry in the series of isomeric DITFBs indicated the more complex nature of the melting process and suggest further physico-chemical investigation of the molecular mechanisms of this fundamental process.

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**Data Availability Statement:** Computational results in \*.CXP format (Crystal Explorer 21.5) are freely available from the authors upon request.

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Conflicts of Interest: The authors declare no conflict of interest.



Appendix A

**Figure A1.** In situ crystal growth setup: Mylar<sup>®</sup> capillary filled with liquid 1,3-DITFB, mounted on goniometer head.



**Figure A2.** Structural overlay of 1,3-DITFB molecule in the native crystal (red) vs. the one found in one of its (randomly picked from CSD) co-crystals with 4-cyanopyridine (CSD ref. NUBTAI, [47], plotted in orange).



**Figure A3.** Fragments of 1,3-DITFB crystal lattice, showing its packing along c (**a**) and b (**b**) crystallographic axis. Blue dashed lines show short contacts: I…I (**a**) and F…C (**b**). Notice its layered structure along c and herringbone structure along b axis.



Figure A4. F…C and I…Cl contacts in the 1,3-DITFB native crystal.

- a. Their geometry (see Table A1).
- b. F…C (green dashed lines) and I…Cl (red dashed lines) contacts and their energy (total intermolecular interaction energy, CE-B3LYP/DGDZVP, kJ/mol)

**Table A1.** Selected intermolecular distances in 1,3-DITFB, Å and their shortening normalized to respective vdW radii sums.

Contact	Distance (d), Å	d Normalized to vdW Radii Sum * d-Σ(vdW Radii)/Σ(vdW Radii)
F1…C6	3.29	-0.03801
F1C5	3.1	-0.09357
F1…C4	3.29	-0.03801
F2…I1	3.97	+0.067204
F4…I2	3.97	+0.067204
F3…C1	3.29	-0.03801
F3…C2	3.02	-0.11696
F3…C3	3.29	-0.03801
F4…I2	4.4	+0.182796
F2…I1	4.4	+0.182796

 $* C_{sp2} \cdots F vdW radii [29] sum (1.87 + 1.55) Å = 3.42 Å. * I \cdots F vdW radii [29] sum (2.17 + 1.55) Å = 3.72 Å.$ 



**Figure A5.** Hirshfield surface (*d<sub>norm</sub>*) showing short F…C contacts in the 1,3-DITFB native crystal.



**Figure A6.** F…C and I…Cl contacts in the 1,3-DITFB native crystal.

- a. Their geometry (see Table A2)
- b. F…C (green dashed lines) and I…Cl (red dashed lines) contacts and their energy (total intermolecular interaction energy, CE-B3LYP/DGDZVP, kJ/mol)

**Table A2.** Selected intermolecular distances in 1,3-DITFB, Å and their shortening normalized to respective vdW radii sums.

Contact	Distance ( <i>d</i> ), Å	d Normalized to vdW Radii Sum * d-Σ(vdW Radii)/Σ(vdW Radii)
F3…C2	3.17	-0.0731
F1C5	3.15	-0.07895
F2…I2	3.69	-0.00806
$F4\cdots I1$	3.69	-0.00806

 $\overline{C_{sp2}}$ ···F vdW radii [29] sum (1.87 + 1.55) Å = 3.42 Å. I···F vdW radii [29] sum (2.17 + 1.55) Å = 3.72 Å.



**Figure A7.** The energy frameworks (CE-B3LYP/DGDZVP) of a fragment of 1,4-DITFB lattice showing total energy (blue tubes, kJ/mol). Cutoff 5 kJ/mol. Notice that total energy correlates with the number of short interatomic I···F and C···F contacts.



**Figure A8.** The energy frameworks (CE-B3LYP/DGDZVP) of a fragment of 1,4-DITFB lattice showing (a) electrostatic energy contribution (red tubes), (b) dispersion energy contribution (green tubes) and (c) total energy (blue tubes). Cutoff 5 kJ/mol.

Notice that electrostatic interactions are comparatively weak (compared to dispersion), and the major contribution to the total energy framework pattern is from the dispersion energy. Table A1 below shows the same pattern (just compare the columns for  $E_{electrostatic}$  (highlighted in red) and  $E_{dispersion}$  (highlighted in green);  $E_{total}$  is highlighted in blue.

Ν	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	x + 1/2, -y + 1/2, -z + 1/2	4.7	B3LYP/DGDZVP	-11.4	-0.5	-29.4	23.1	-23.7
4	-x + 1/2, -y, z + 1/2	9.19	B3LYP/DGDZVP	-7.5	-0.5	-9.3	15.3	-6.9
2	x + 1/2, -y + 1/2, -z + 1/2	6.45	B3LYP/DGDZVP	-4.2	-0.5	-16.2	9	-13.4
2	x, y, z	5.91	B3LYP/DGDZVP	-9.4	-0.5	-22.7	16.7	-19.7
2	-x, -y, -z	9.90	B3LYP/DGDZVP	-0.1	0	-2.5	0.5	-1.9
2	-x, -y, -z	9.09	B3LYP/DGDZVP	-2.9	-0.2	-8.2	6.1	-6.6

Table A3. Interaction Energies (kJ/mol).

R is the distance between molecular centroids (mean atomic position) in Å. Total energies are the sum of the four energy components, scaled appropriately (see the scale factor Table A4 below). Scale factors benchmarked for CE-B3LYP/6-31G(d,p) energy model [61] can be used for CE-B3LYP/DGDZVP [62].

 Table A4. Scale factors.

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP/6-31G(d,p)	1.057	0.74	0.871	0.618

**Table A5.** Comparison of experimental  $\Delta H_{\text{sublimation}}$  and calculated  $E_{\text{lattice}}$  for *para*-dihalobenzenes.

Compound	$\Delta H_{sublimation}$ Experimental [63]	<i>E</i> <sub>lattice</sub> Calculated in This Work (B3LYP/DGDZVP)
1,4-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	64.8 at 298 K [63] 65.2 at 313 K [64] 56.9 at 304 K [64]	-58.3
$1/4-C_{6}H_{4}Br_{2}$	73.3 at 313 K [65] 74.5 at 298 K [63,66]	-74.5
1,4-C <sub>6</sub> H <sub>4</sub> I <sub>2</sub>	63.4 at 386 K [65] ** 85.4 at 298 K [63,66]	-83.7

<sup>\*\*</sup> Note that  $\Delta H_{subl}$  for 1,4-C<sub>6</sub>H<sub>4</sub>I<sub>2</sub> is reported for 372–401 K range [65] which is close to 1,4-C<sub>6</sub>H<sub>4</sub>I<sub>2</sub> melting point (403 K). According to a recent critical evaluation [67] of the method used by Chickos et al. [68,69] for the estimation of notable errors in the evaluation of sublimation, enthalpies may occur in the vicinity of the melting temperature (Table A6). Therefore, we may suspect that calculated  $E_{\text{lattice}}$  value -83.7 kJ/mol is more adequate. It fits well with the reasonable trend of increasing  $\Delta H_{\text{subl}}$  as we move from 1,4-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> to 1,4-C<sub>6</sub>H<sub>4</sub>I<sub>2</sub> and experimental  $\Delta H_{\text{subl}}$  reported by Solomonov, Verevkin et al. [63,66].

Table A6. Meting points for ortho-, meta- and para-substituted benzenes (literature data, experimental).

Compound	Melting Point m.p. °C
1,2-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	-17
1,3-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	-24
$1,4-C_6H_4Cl_2$	53
$1,2-C_6H_4Br_2$	7
$1,3-C_6H_4Br_2$	-7
$1,4-C_{6}H_{4}Br_{2}$	87
$1,2 C_6 H_4 I_2$	27
$1,3 C_6 H_4 I_2$	35
$1,4 C_6 H_4 I_2$	130
1,2-xylene	-25
1,3-xylene	-47
1,4-xylene	14

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