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Dedicated to Prof. Ion Grosu
on the occasion of his 70th anniversary

HALOGEN-BONDED CO-CRYSTALS OF AZULENE-1-CARBOXALDEHYDE WITH PERFLUORINATED DIIODOBENZENES

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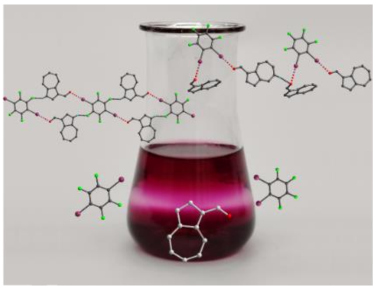
Two new co-crystals assembled from halogen-bonded perfluorinated diiodobenzenes (1,4-ditfb and 1,2-ditfb) and 1-azulenecarboxaldehyde (azcho) are obtained. The crystal structures for both co-crystals show O···I halogen bonds, complemented by weaker C-H···F interactions. The azulene fragment contributes to the stabilisation of the final supramolecular architecture through π-π stacking interactions, highlighting its unique ability to direct the assembly of these co-crystals.



INTRODUCTION

Crystal engineering has become a key component of materials science and supramolecular chemistry, focusing on the design and synthesis of molecular solids with tailored physicochemical properties.[1] The primary principles of this field are rooted in the understanding of intermolecular forces, such as hydrogen bonding, halogen bonding, van der Waals interactions, hydrophobic effects, and π-π stacking.[2] These interactions drive the spontaneous organization of components into supramolecular architectures, which in turn influence the physicochemical properties of the material.[3] Hydrogen bonds have long been recognized as playing a crucial role in the structure and function of molecules, cells, tissues, and material science.[4] Lately, halogen bonds, although firstly suggested in 1863,[5] are emerging as powerful forces to design stable frameworks due to their directionality and to the fact that their strength can be tuned by the choice of the halogen atom (*e.g.* iodine *vs*. bromine).[6] This type of interaction occurs between a region of electrophilicity attached to a halogen atom, such as chlorine, bromine or iodine, in one molecule, and a nearby electron-rich site, often a nitrogen or oxygen atom, in another molecule.[7] Consequently, the study of halogen bonds has become a significant area of interest in crystal engineering with numerous reports of halogen bonded systems exhibiting a wide range

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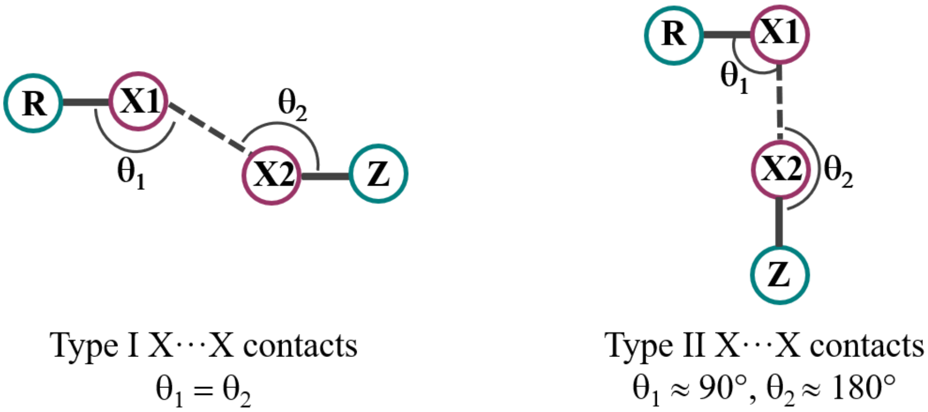
of applications, including anion receptors,[8] organocatalysts,[9] magnetic materials,[10] liquid crystals,[11] etc. Generally, two types of halogen R–X1···X2–Z interactions have been described in halogen-bonded assemblies, namely Type I contact when θ1 (R–X1···X2) ≈ θ2 (X1···X2–Z), respectively, Type II, when θ1 ≈ 90° and θ2 ≈ 180° (Scheme 1).[12]



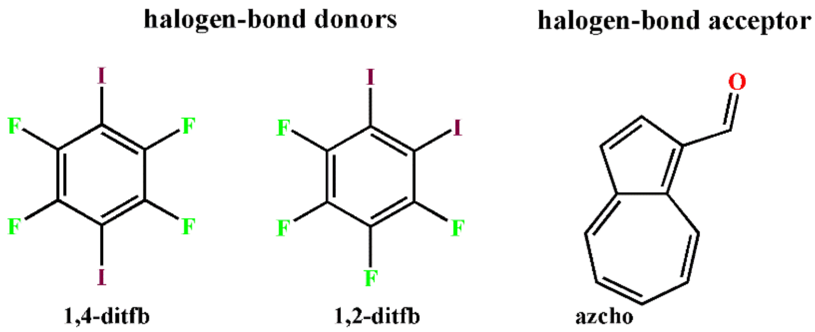
Scheme 1 – Halogen interactions R–X1···X2–Z in assemblies with halogen bonds.

Numerous halogen-bonded co-crystals are based on the interactions between strong halogen bond donors and strong nitrogen-based acceptors, with a particular emphasis on pyridine nitrogen atoms,[13] while others, such as carbonyl, nitro, methoxy or hydroxy1 groups, are less investigated.[14] Though, fascinating supramolecular architectures were reported involving the aldehyde group oxygen atom as an efficient halogen bond acceptor in competition with the hydroxy, methoxy and pyridine groups, forming bifurcated hydrogen and halogen bonding.[15] Our research group has utilized azulene derivatives as key components in the assembly of supramolecular structures, yielding materials with fascinating properties.[16,18] The azulene units served as key organizational elements, facilitating the assembly and stabilization of supramolecular aggregates through π-π stacking interactions.[17,18] Recently, we introduced for the first time 1,3-azulenedicarboxaldehyde as halogen-bond acceptor with 1,2-diiodotetrafluorobenzene (1,2-ditfb), 1,4-diiodotetrafluorobenzene (1,4-ditfb) and 1,3,5-triiodotrifluorobenzene (1,3,5-titfb) as donor components.[19] Besides, primarily linear halogen I···O bonds, C–H···O hydrogen bonds and π–π interactions of the azulene moieties were observed.[17] The incorporation of azulene moiety into the supramolecular aggregates confers to the assembled structures new properties. Azulene exhibits a unique combination of properties, including its intrinsic bipolar character, anomalous $S_2 \rightarrow S_0$ fluorescence, and redox behavior,[20] making it an attractive building block for the design of multifunctional molecular materials[21,22] and azulene-based polymers.[23]

Seeking to further explore the potential of azulene-based co-crystals, we have turned our attention to the synthesis and characterization of new halogen-bonded co-crystals of 1-azulenecarboxaldehyde (azcho) with 1,2-diiodotetrafluorobenzene (1,2-ditfb) and 1,4-diiodotetrafluorobenzene (1,4-ditfb). We report herein, the X-ray crystal structures and the spectroscopic characterization of two new co-crystals, with focus on the role of azulene moiety in the crystal packing.

RESULTS AND DISCUSSION

The cocrystallization processes are similar to our previous studies,[19] namely, they consist of mixing the solutions of the two components, in equimolar ratio, at room temperature. The molecular structure of the used ditopic perfluorobenzenes and azulene-1-carboxaldehyde are represented in Scheme 2. The co-crystals were first characterized by IR spectroscopy. For both of them, the IR spectrum contains the bands of the precursors with small shifts of the relevant vibrations. As such, the $\nu_{C=O}$ stretching vibration of the free azcho is present at 1645 cm^{-1}, shifted approximatively by 20 cm^{-1} in co-crystals **1** and **2**, respectively. Small differences are also observed for the C=C stretching vibrations in the 1400–1500 cm^{-1} region as compared to those in the corresponding spectrum of free donor and acceptor molecules.



Scheme 2 – Chemical structures of the halogen bond donors and acceptor used in this study.

Co-crystallization of azcho and 1,4-ditfb from a methanol/chloroform solution yielded co-crystal **1** - $(azcho)_2$(1,4-ditfb). This crystallizes in the triclinic *P-1* space group with the asymmetric unit containing one azcho molecule and one-half molecule of 1,4-ditfb (Fig. 1). The molecules are linked by almost linear I···O halogen bond (∠C–I···O angle of 176.06°) involving the carbonyl oxygen atom and the iodine atom, assembling a three-molecular motif. The intermolecular I···O interaction is of 2.873 Å which corresponds to *ca*. 18% reduction of the sum of the van der Waals radii for O and I atoms. Further on, the presence of F atoms promotes the formation of C–H···F type hydrogen bonds (C2b···F1 = 3.414 Å), that organizes the three-component halogen-bonded assemblies into 2D layers (Fig. 2). Table 1 provides the summary of the crystallographic data together with refinement details. Additional details concerning hydrogen and halogen bond metrics are presented in Tables 2 and 3.

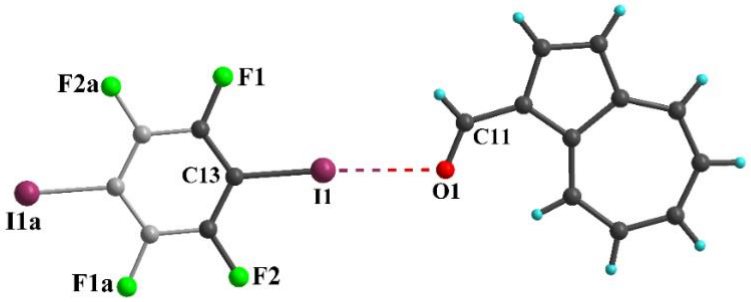


Fig. 1 – Asymmetric unit of co-crystal **1** with selected atom labelling. Symmetry operations: ^{a} = –*x*, 1–*y*, 2–*z*.

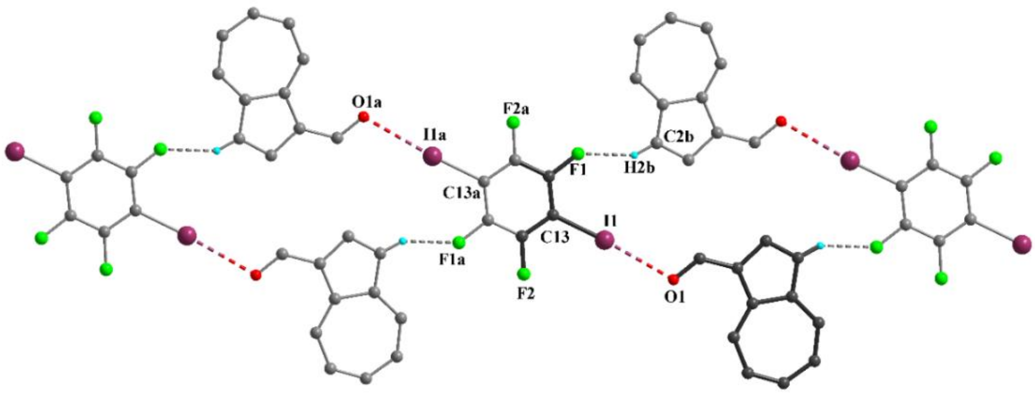
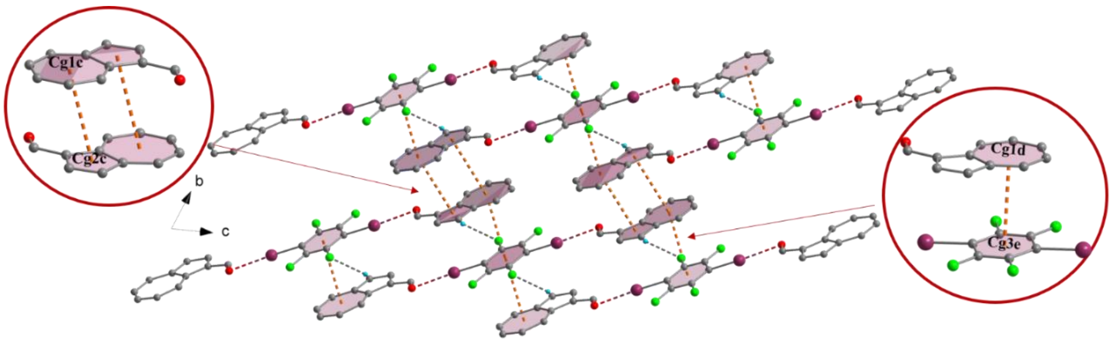
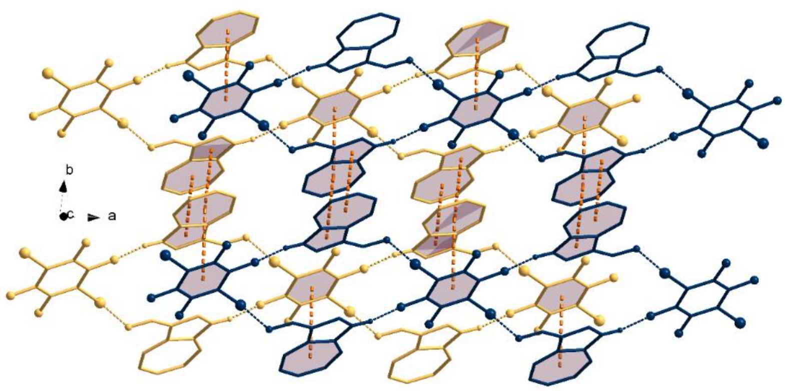


Fig. 2 – Crystal packing diagram of co-crystal **1**. Symmetry operations: ^{a} = –*x*, 1–*y*, 2–*z*, ^{b} = 2–*x*, 1–*y*, 1–*z*. Non-relevant H atoms were omitted for clarity.

Adjacent 2D layers are further packed within the crystal *via* π-π stacking interactions established between the seven-membered rings and the five-membered rings belonging to the azulene (according to its preferred polarization), and also between benzene and azulene units, thus giving rise to a three-dimensional supramolecular architecture (Figs. 3a and b).



a)

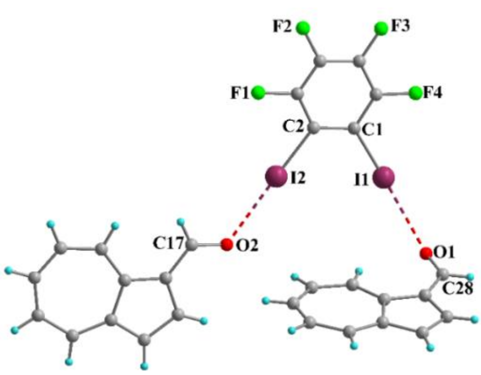


b)

Fig. 3 – Crystal packing diagram of **1** showing the: a) supramolecular network assembled via π-π interactions, as viewed along crystallographic *a* axis (centroid-to-centroid distances are drawn in dashed-orange lines); b) 3D network assembled *via* π-π interactions of Cg1c···Cg2c = 3.78 Å and Cg1d···Cg3e = 3.77 Å. Symmetry operations: ^{c} = –1+*x*, *y*, *z*,^{d} = –1–*x*, 1–*y*, 1–*z*,^{e} = -2+*x*, 1+*y*, 1+*z*.

Cocrystallization of azcho with 1,2-ditfb yielded co-crystal **2**-$(azcho)_2$(1,2-ditfb), which crystallizes in the same triclinic system, with asymmetric unit containing one 1,2-ditfb molecule and two azcho molecules connected *via* I···$O_{carbonyl}$ halogen bonds (∠C1–I1···O1 = 173.31º, ∠I1···O1–C28 = 121.30º, ∠C2–I2···O2 = 178.44º and ∠I2···O2–C17 = 121.29º) (Fig. 4a). The I···$O_{carbonyl}$ distances are 3.041 Å (I1···O1) and 2.884 (I2···O2), corresponding to 14 %, respectively 18% reduction of the sum of the van der Waals radii for O and I atoms. The C–I···O angles are nearly linear 173.31° and 178.44°, respectively. The three-component halogen bonded assemblies further connect with each other *via* C–H···O hydrogen bonds, leading to supramolecular chains of herringbone type motifs (Fig. 4b). Crystallographic data and refinement details are provided in Table 1, while hydrogen and halogen metrics are gathered in Tables 2 and 3.

a)



b)

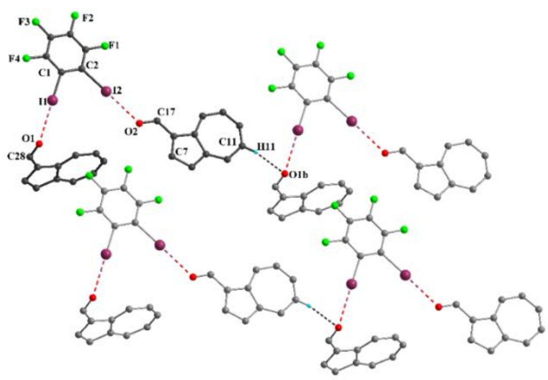


Fig. 4 – a) Asymmetric unit of co-crystal **2** with selected atom labelling; b) crystal packing diagram showing the C-H···O hydrogen bonds drawn as black-dashed lines. Symmetry code^{b} = *x*, *y*, +*z*–1.

Adjacent chains are interacting *via* interchain CH···π interactions established between azulene moieties C13–H13···Cg1c [C13–H 0.93 Å, H···Cg1c 3.03 Å, C13···Cg1c 3.89 Å, ∠C6–H···Cg1c 155.20°] (Fig. 5), while *offset* π-π interactions established between benzene and the five membered rings of azulene units (3.46 and 3.86 Å), give rise to a 3D-architecture (Fig. 6). Detail of CH···π and π-π interactions within crystal structure of **2** are depicted in Fig. 7.

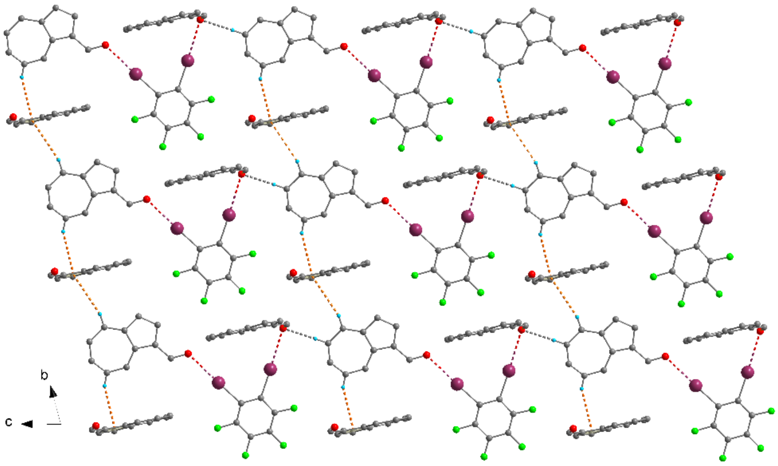


Fig. 5 – 2D supramolecular sheet observed in co-crystal **2**, as viewed along crystallographic *a* axis.

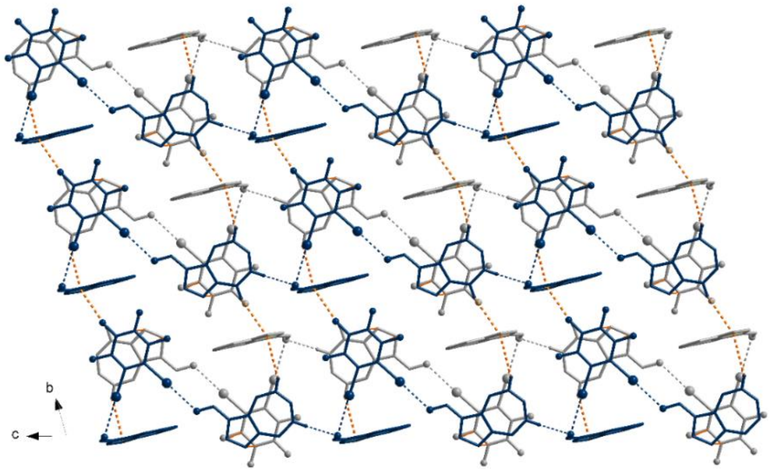


Fig. 6 – Crystal packing of co-crystal **2**, showing the supramolecular network assembled via CH···π and π-π interactions drawn as dashed orange line, viewed along crystallographic *a* axis.

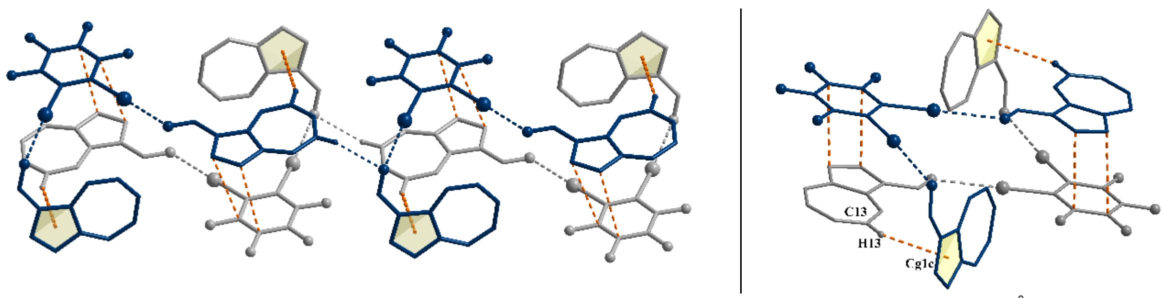


Fig. 7 – Detail of CH···π and π-π interactions within crystal structure of **2**, C13···Cg1c 3.89 Å. Symmetry code[c] = 1–*x*, 2–*y*, 2–*z*

Owing to the presence of azulene moiety, the two co-crystals are colored, with strong absorption bands in the UV-Vis spectra. The solid-state electronic spectra were recorded using the diffuse reflectance technique and are shown in Figure 8. In both cases, well-defined absorption peaks are observed between 200–400 nm region and the azulene characteristic visible S_0–S_1 absorption band. This last band is sensitive to the substitution and is observed at 537 nm, with shoulder at 624 nm, for co-crystal **1**, and 524 nm, with the shoulder at 621 nm for co-crystal **2**, slightly shifted in comparison with free azcho (530 nm, with a shoulder at 628 nm).

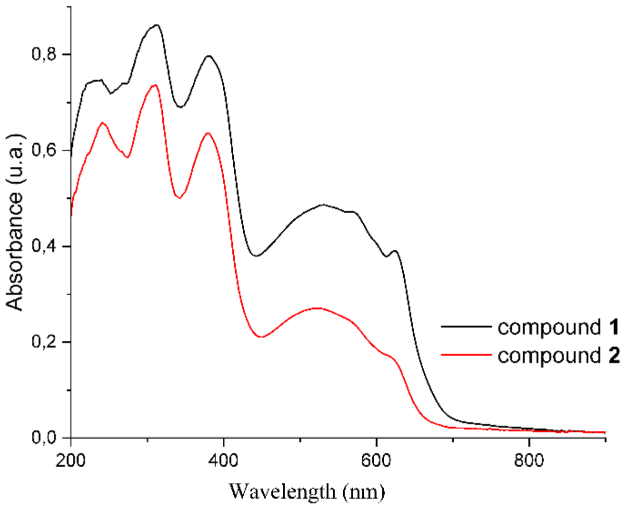


Fig. 8 – Electronic spectra recorded for **1** and **2**.

To conclude, following our previous study where we described the halogen bonding of 1,3-azulenedicarboxaldehyde with ditopic perfluorinated benzenes, in this work we have explored the ability of the mono-aldehyde oxygen atom of azulene-1-carboxaldehyde to act as a halogen bond acceptor for co-crystal formation. The herein prepared halogen-bonded co-crystals, together with the previously reported structures,[19] demonstrate that azulene-aldehydes are reliable halogen bond acceptors in engineering halogen bonded solids.

Table 1

Crystal data and structure refinement for co-crystals **1** and **2**

Co-crystal	**1.**	**2.**
empirical formula	$C_{14}H_8F_2IO$	$C_{28}H_{16}F_4I_2O_2$
Fw	357.10	714.21
T [K]	293	293
System	triclinic	triclinic
space group	*P-1*	*P-1*
a [Å]	6.8972(4)	7.4075(3)
b [Å]	9.4881(4)	10.9390(5)
c [Å]	10.6490(6)	16.3341(8)
α [°]	66.997(5)	74.553(4)
β [°]	78.506(5)	88.448(4)
γ [°]	82.982(4)	86.217(3)
V [Å^3]	627.8(1)	1272.92(10)
Z	1	2
ρ_{calcd} [g cm^{-3}]	1.889	1.863
μ [mm^{-1}]	2.558	2.524
2Θ range	4.21 to 50	3.87 to 50
Reflections collected	6260	15405
Independent reflections	2017 [R_{int}= 0.0371]	4472 [R_{int}= 0.0393]
Data/restraints/parameters	2212/0/163	4472/0/334
R_1[a]	0.0237	0.0413
wR_2[b]	0.0557	0.1139
GOF[c]	1.068	1.027
Largest diff. peak/hole / e Å^{-3}	0.37/–0.34	1.07/–0.65

Table 2

Halogen bonds parameters for co-crystals **1** and **2**

Co-crystal	D···A	d(DA)/ Å	∠(C – D···A)/°	∠(D···A-C)/°
1.	I1···O1	2.873	176.06	112.23
2.	I1···O1	3.041	173.31	121.30
	I2···O2	2.884	178.44	121.29

Table 3

Selected hydrogen bonding metrics for co-crystals **1** and **2**

Co-crystal	D-H···A	d(DH)/Å	H···A/Å	D···A/Å	∠(D H···A)/°
1.	C2b – H2b···F1 ^{b} = 2-*x*, 1-*y*, 1-*z*.	0.93	2.642	3.414	140.90
2.	C11–H11···O1b ^{b} = *x*, *y*, +*z*–1	0.93	2.552	3.442	160.29

EXPERIMENTAL

Materials and methods

Commercially available reagents were used without further purification; 1-azulenecarboxaldehyde was synthesised following reported procedure.[24] IR (KBr), υ 2804 (w), 2733 (m), 1645 (s), 1498 (s), 1414 (s), 1395 (s), 1279 (m), 1021 (m), 797 (m), 742 (m), 641 (w), 569 (w) cm^{-1}; UV-Vis (MgO): 224, 308, 379, 530 and 628 (shoulder) nm.

Co-crystal 1 – (azcho)$_2$(1,4-ditfb)

To a solution of 1-azulenecarboxaldehyde (17 mg, 0.11 mmol) in 10 mL $CHCl_3$ was added 1,4-diiototetrafluorobenzene (43 mg, 0.11 mmol) dissolved in methanol (10 ml). The resulting mixture was stirred at room temperature for three hours. Dark purple crystals were obtained by slow evaporation at room temperature in two days, yield 35 % yield (27 mg). IR (KBr), υ 2745 (w), 2364 (m), 1625 (s), 1458 (s), 1403 (m), 1267 (m), 1200 (m), 942 (m), 792 (m), 740 (m), 636 (w), 656 (w) cm^{-1}; UV-Vis (MgO): 232, 311, 380, 537 and 624 (shoulder) nm.

Co-crystal 2 – (azcho)$_2$(1,2-ditfb)

To a solution of 1-azulenecarboxaldehyde (17 mg, 0.11 mmol) in $CHCl_3$ (10 ml) was added 1,2-diiototetrafluorobenzene (43 mg, 0.1 mmol) dissolved in methanol (10 ml). The resulting mixture was stirred at room temperature for three hours, and let to stand at room temperature. Purple crystals were obtain by slow evaporation at room temperature in four days, in 32% yield (25 mg). IR (KBr), υ 2750 (w), 2353 (m), 1623 (s), 1484 (s), 1424 (m), 1268 (m), 1204 (m), 1097 (w), 1011 (m), 795 (m), 751 (m), 639 (w), 557 (w) cm^{-1}; UV-Vis (MgO): 241, 309, 379, 524 and 621 (shoulder) nm.

Physical measurements and X-ray crystallography

IR spectra (KBr pellets) were recorded on a Tensor 37 spectrophotometer in the 4000–400 cm^{-1} region and UV-Vis spectra were recorded with a Jasco V-670 spectrophotometer. X-ray diffraction measurements for the all crystals were performed on a Rigaku XtaLAB Synergy-S diffractometer operating with Mo- Kα (λ = 0.71073 Å) micro-focus sealed X-ray tube. The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-2014 or SHELX-2018 crystallographic software package.

The CCDC reference numbers for co-crystal 1 and 2 are 2415809 and 2415810. The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Center vfia http://www.ccdc.com.ac.uk/structures/

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