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Penta- and Decafluorinated Dibenzalacetones: Synthesis, Crystal Structure, and Cocrystallization Experiments

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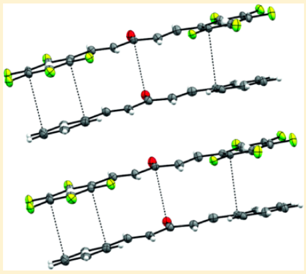
Supporting Information

ABSTRACT: The nonfluorinated parent dibenzalacetone **1** as well as the corresponding penta- (**2**) and decafluorinated (**3**) derivative compounds were prepared, crystallized, and subjected to co-crystallization experiments. Only **3** yielded a 1:1 co-crystal with **1**, while **2** did not form co-crystals with either **1** or **3**. Powder X-ray diffraction patterns were determined to verify the co-crystallization experiments. The influence of the fluorine on the molecular geometry and crystal packing were studied and comparatively discussed. Conclusions with reference to the priority of Ar···Ar^F contact modes in the crystalline packing being in competition with other fluorine and non-fluorine involved supramolecular interactions were drawn.



INTRODUCTION

Noncovalent interactions of fluorinated compounds in the solid state have been investigated and reviewed in the last few decades.[1−6] Regarding the fluorine-involved interactions, different modes are discussed: (1) C−H···F, (2) C−F···F, (3) C−F···C(=O), (4) C−F···Ar^F, and (5) the most relevant Ar···Ar^F. Nevertheless, all fluorine-containing interactions including Ar···Ar^F are rather weak and still under controversial discussion.

As presently seen, the Ar···Ar^F interaction is a stabilizing contact that occurs between a perfluorinated and a non-fluorinated aromatic ring.[2,3,5] The distances between adjacent centers of the rings are in the range of 3.4−4.8 Å with ring-plane angles up to 20°.[2] This kind of interaction is not only used for the generation of molecular stacks in crystal engineering[7,8] but is also a well-known supramolecular synthon[2,3,5,9] being profitable in the solid state [2 + 2] photocycloaddition.[10,11] Moreover, it offers advantages for the optical and electronic properties of organic compounds[12] and is used in the design of liquid crystals[13] and π-gels.[14] Two models are discussed in the recent literature to explain and quantify the Ar···Ar^F interaction. The first is based on polarization of the π-system,[15,16] while the second is derived from substituent effects.[17,18] Considering this element of uncertainty, a multitude of co-crystals generated by a perfluorinated and a non-fluorinated aromatic ring have been described. Furthermore, stacking interactions in isolated structures have been observed.[10,19−25]

In addition, significance of the C−F···H−(O,N) type hydrogen bonding is currently discussed rather intensely and controversially as well.[26−30] Previous studies regarding investigations of C−H···F and C−F···F contacts have reported mainly on molecular systems without strong hydrogen donors and acceptor groups. Instead crystal structure investigations on cyclic imides,[31,32] benzophenones,[33] pyridines,[34] benzonitriles,[35] benzylideneanilines[36,37] and aromatic azo compounds[38,39] are reported. Examples of rarely described compounds with strong hydrogen donor and acceptor groups such as OH, COOH, and NH/NH_2 are benzanilide,[40] phenylureas,[41] amines,[42] and fluorinated anilines.[43−46] With reference to the Ar···Ar^F interaction, steric hindrance, large torsion angles between adjacent phenyl rings, and bulky substituents favor C−H···O and C−H···F contacts at the expense of Ar···Ar^F stacking.[33,47] Furthermore, it has also turned out that a planar environment of the molecule is not an absolute requirement for Ar···Ar^F interaction but preferable. In short, conditions enabling a sure prediction of Ar···Ar^F formation in a crystal packing being in competition with other interaction modes are still rather shaky, requiring more examination.

Here, we present the synthesis and crystal structure analyses of the compounds **1**−**3** (Scheme 1) which could make a contribution for investigating this question. They refer to fluorinated dibenzalacetones **2**−**3** deriving advantage from (1) an expected almost planar molecular geometry based on the π-conjugation and promoting the formation of Ar···Ar^F stacks and (2) the possibility to have one or two perfluorinated aryl rings. In addition, we include the unfluorinated parent compound **1** in the study considering reasonable structural comparison and also to probe feasibility of co-crystallization between fluorinated and unfluorinated species. All this is subject to an interplay between C−H···O, C−H···F, C−H···π, C−F···π^F, F···F, and Ar···Ar contacts competing with the Ar···Ar^F interaction under discussion.

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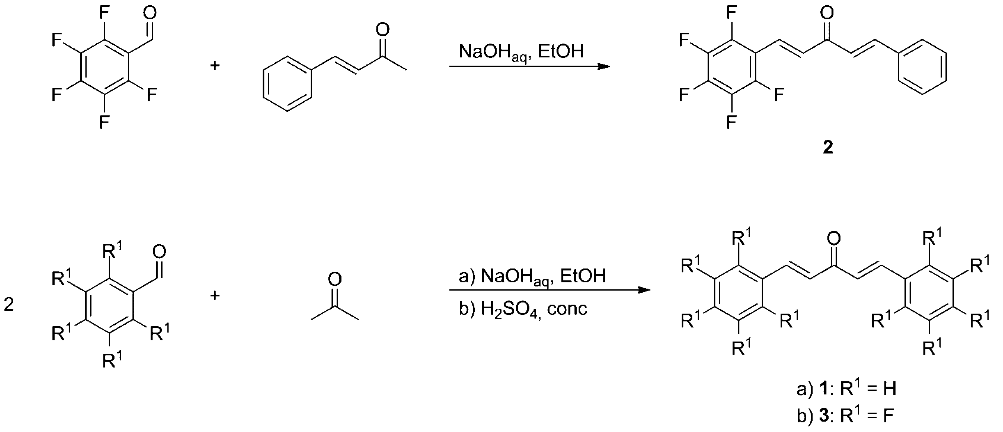
Scheme 1. Preparation of Dibenzalacetones 1−3



EXPERIMENTAL SECTION

General Remarks. Melting points (uncorrected) were determined using a microscope heating stage PHMK Rapido (VEB Wägetechnik). IR spectra were measured on a FT-IR 510 Nicolet as KBr pellets. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in chloroform solution at room temperature on a Bruker Avance DPX 400 at 400, 100, and 376 MHz, respectively. The splitting of proton and carbon resonances is defined as s = singlet, d = doublet, t = triplet, and m = multiplet. Resonances are assigned according to the calculation of increments of groups. The same numbering is used as for the crystallographically determined molecular structure (Figure 2). Elemental analyses were performed on a Heraeus CHN rapid analyzer. Mass spectra were obtained using a Hewlett-Packard GC-MS 5890. Powder diffraction data were recorded on a Siemens D5000 at room temperature.

Materials. Organic solvents were purified by standard procedures. Starting compounds 2,3,4,5,6-pentafluorobenzaldehyde (98%) and benzaldehyde (98%) were purchased from ABCR (Germany). 4-Phenylbut-3-en-2-one[48] and dibenzalacetone **1**[49] were prepared according to the literature procedures using NaOH in a water−ethanol mixture.

Synthesis. *Synthesis of 1-Phenyl-5-(2,3,4,5,6-pentafluorophenyl)penta-1,4-dien-3-one,* ***2.*** A solution of sodium hydroxide (1.24 g, 31.0 mmol) in 15 mL of water and 12 mL of ethanol, 2,3,4,5,6-pentafluorobenzaldehyde (5.00 g, 25.0 mmol), and 4-phenyl-but-3-en-2-one (3.65 g, 25.0 mmol) was stirred for 30 min at room temperature. The solid raw product was collected by suction filtration and washed with water to remove the sodium hydroxide. Recrystallization from *n*-hexane yielded 3.50 g (43%) of a yellow crystalline powder. Mp 154−155 °C (from *n*-hexane). Found: C, 63.08; H, 2.96; $C_{17}H_9F_5O$ requires C, 62.97; H, 2.80%. ν_{max} (KBr)/cm^{-1} 3063 (w, CH_{Ar}), 1674 (s, C═O), 1612 (m, C═C), 1594 (s, Ph); δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 7.78−7.38 (8H, m, Ph, HC═C*H*Ph), 7.02 (1H, d, $^3J_{HH}$ = 16.0 Hz, *H*C═CHPh); δ_C (100 MHz; CDCl$_3$; Me$_4$Si) 188.1 (s, C═O), 144.9, 147.3 (d, $^1J_{CF}$ = −238.4 Hz, C1/C5), 144.7 (s, C═CPh), 140.4, 143.0 (d, $^1J_{CF}$ = −258.5 Hz, C3), 136.6, 139.2 (d, $^1J_{CF}$ = −257.5 Hz, C2/C4), 134.4 (s, C12), 131.8 (t, $^3J_{CF}$ = −6.9 Hz, C═CPhF$_5$), 130.9 (s, C═CPh), 129.0 (s, C13/C17), 128.6 (s, C14/C16), 126.5 (s, *C*═CPhF$_5$), 125.6 (s, C15), 110.4 (t, $^2J_{CF}$ = 13.4 Hz, C6); δ_F (376 MHz; CDCl$_3$) −139.8 (2F, m, F1/F5), −151.8 (1F, m, F3), −162.3 (2F, m, F2/F4); *m/z*: 324 [M]$^+$, 323, 193, 103.

Synthesis of 1,5-Bis(2,3,4,5,6-pentafluorophenyl)penta-1,4-dien-3-one, ***3.*** A solution of 2,3,4,5,6-pentafluorobenzaldehyde (5.0 g, 25.0 mmol) and acetone (0.73 g, 12.5 mmol) in 25 mL of sulfuric acid was stirred for 4 days at room temperature. Sulfuric acid (5 mL) was added and the mixture was stirred for 5 additional days. After the mixture was carefully quenched on ice, the solid was separated via suction filtration and recrystallized from *n*-hexane to yield 1.71 g (33%) of a yellow crystalline solid. Mp 125 °C (from *n*-hexane; lit.[50] 127−129 °C). Found: C, 49.25; H, 1.24; $C_{17}H_4F_{10}O$ requires C, 49.30; H, 0.97%. ν_{max} (KBr)/cm^{-1} 3032 (w, C$_{Ar}$H), 1680 (s, C═O), 1618 (s, C═C), 1523 (s, Ph), 1497 (s, Ph). δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 7.71 (2H, d, $^3J_{HH}$ = 16.4 Hz, HC═C*H*Ph), 7.31 (2H, d, $^3J_{HH}$ = 16.4 Hz, *H*C═CHPh); δ_C (100 MHz; CDCl$_3$; Me$_4$Si) 187.5 (s, C═O), 144.7, 147.2 (d, $^1J_{CF}$ = −251.5 Hz, C1/C5/C13/C17), 140.7, 143.3 (d, $^1J_{CF}$ = −258.5, C3/C15), 136.6, 139.1 (d, $^1J_{CF}$ = −254.5 Hz, C2/C4/C14/C16), 131.7 (s, C═CPh), 127.8 (*C*═CPh, s), 110.0 (t, $^2J_{CF}$ = 13.4 Hz, C6/C12); δ_F (376 MHz; CDCl$_3$) −139.4 (m, 4F, F1/F5/F6/F10), −150.8 (m, 2F, F3/F8), −161.9 (m, 4F, F2/F4/F7/F9); *m/z*: 414 [M]$^+$, 395, 221, 193, 143.

Crystal Preparation and Crystal Structure Determination. Single crystals of **2**, **3**, and **1·3** were obtained by isothermal evaporation of solutions of ethanol (**2**) and chloroform (**3**, **1·3**) at room temperature. In an optically opaque sample tube 0.4 mmol of **2** (0.13 g, 0.4 mmol), **3** (0.16 g, 0.4 mmol), **1** (0.09 g, 0.4 mmol), and **3** (0.16 g, 0.4 mmol) were dissolved in ethanol (**2**) or chloroform (**3**, **1·3**). All crystals were measured on a Bruker Kappa Apex II using graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). Software for data collection: SMART Version 5.628,[51] cell refinement: SMART Version 5.628[51] and data reduction: SAINT Version 6.45a.[51] Preliminary structure models were derived by Direct Methods using the SHELXTL package[52,53] and were refined by full-matrix least-squares calculation based on F^2 for all reflections.[52,54] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the models in calculated positions and were refined as constrained to bonding atoms. The crystal data and experimental parameters are given in the References.[55]

RESULTS AND DISCUSSION

Synthesis. Dibenzalacetones as representative of the substance class of α,β-unsaturated carbonylic compounds are normally accessible via Claisen−Schmidt reaction involving the addition of a C−H acetic reagent to a carbonylic carbon atom followed by dehydratization (Scheme 1).[56,57] This reaction commonly requires a basic catalyst, for instance, sodium hydroxide dissolved in ethanol which is used for compounds **1** and **2**. However, using NaOH as the base was found unsuitable for the synthesis of the decafluorinated derivative **3** due to the nucleophilic attack of the hydroxide at the aromatic ring. Mikhalina and Fokin described the synthesis of **3** applying gaseous hydrogen chloride for several days.[50] In exchange for this acidic medium, stirring of the reaction compounds in concentrated sulfuric acid at room temperature for 4 days was applied, which was a more agreeable procedure in handling. Here, sulfuric acid acts both as proton donor and hygroscopic medium.

Crystal Preparation. Single crystals suitable for diffraction measurements were achieved via isothermal evaporation of solutions of ethanol (**2**) and chloroform (**3**). In order to study the potential behavior of the different compounds to form co-crystals that might be stabilized by Ar⋯Ar^F stacking interactions, all possible 1:1 combinations of the dibenzalacetones **1**−**3** were dissolved in an equimolar ratio in chloroform and crystallized from this solvent. The crystalline samples obtained from each of the crystallization experiment were subjected to unit cell measurements at 93 K using 15 single crystals of each crystal batch. As a result of this analysis, it is shown that only the combination of **1** and **3**, i.e., the 1:1 mixture of the non-fluorinated parent compound **1** and the decafluorinated derivative **3**, gave rise to the formation of the 1:1 stoichiometric co-crystal **1·3**, whereas the other two combinations (**1·2** and **2·3**) failed yielding only a mixture of crystals of the single components.

Nevertheless, the 1:1 co-crystal **1·3** seems not to be a favored crystal phase. Single crystals in this connection were either identified as **1·3** or the isolated components **1** or **3**. The XRD pattern determined after the removal of the 15 single crystals (the rest of the sample) is given in Figure 1b. Figure 1a shows the calculated pattern based on the single crystal data of the co-crystal **1·3**, while Figure 1c,d gives the experimental XRD pattern of the isolated components **1** and **3**.

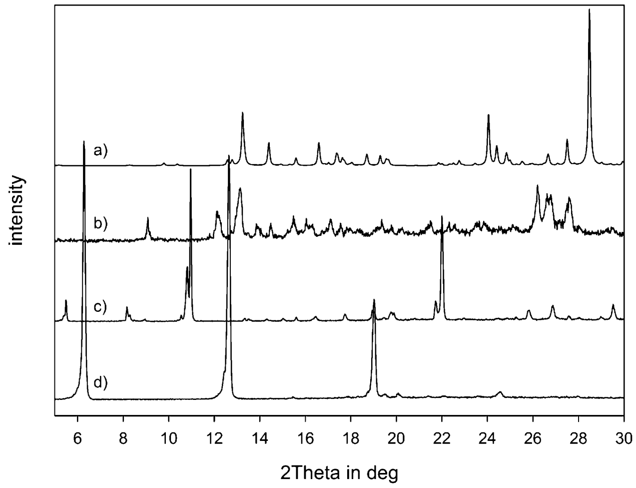


Figure 1. (a) Calculated XRD pattern based on the single crystal data of **1·3**; (b) experimental XRD pattern of the sample from the co-crystallization experiment of **1** and **3**; experimental XRD pattern of the single components of (c) **3** and (d) **1**.

The signal-to-noise ratio of the XRD pattern of co-crystallization phase is very low showing an amorphous character of the bulk material. Though crystallinity is indicated, a clear assignment to a specific phase cannot be drawn. Apparently, different amorphous and crystalline phases are more or less equal during the crystallization process applied in this experiment. It shows that the 1:1 co-crystal does not represent the main product phase and the influence of several aspects on crystallization of a specific phase is significant. Possible aspects are temperature, solvent, and concentration. A similar behavior may be the reason for the failed isolation of co-crystals of **1** with **2** and **2** with **3**. This latter finding is remarkable since **2**, due to its unfluorinated and pentafluorinated aryl units, has a chance to form Ar⋯Ar^F stacking with either **1** or **3**. Finally, the co-crystal **1·3** was found to melt at 180 °C, in contrast to the single components showing a melting point of 127−129 °C (**1**) and 111 (**3**). This thermal behavior was observed earlier, e.g., the 1:1 mixture of benzene and hexafluorobenzene melts at 23.7 °C.[19]

Crystal Structure Description. Compound **1** has been described to show a photoinduced rearrangement depending on UV/vis irradiation and irradiation time.[58] All independent molecules determined in the respective experiment exhibit a molecular disorder. The compound occurs in two different orientations not symmetry related. The isomerism of the olefinic moiety with respect to the C═O bond[58] can be specified as follows: (1) The C−O double bond is orientated almost parallel to the olefinic double bond (∼180°); (2) the angle between the C═O group and the C−C double bond is about 60°. A similar disorder was found in the crystal structure of 1,5-bis(4-fluorophenyl)penta-1,4-dien-3-one in all three independent molecules in the crystal structure.[59] In the current study of **2**, **3**, and **1·3**, however, the non-, penta-, and decafluoro substituted dibenzalacetones, respectively, do not exhibit a disorder.[55] Instead, they show only one isomer with an angle of about 60° between the olefinic and carbonylic double bonds in their crystal structures (Figure 2). In conformity with the behavior of **2**, **3**, and **1·3**, the 2,6,2′,6′-tetrafluoro substituted dibenzalacetone was also reported to crystallize in only one conformational isomer.[60]

The two positions in the disorder of the unfluorinated compound **1** derive from conformational isomerism involving rotation around the C−C bond neighboring the carbonyl group [O(1)−C(9)−C(8)−C(7) and O(1)−C(9)−C(10)−C(11)]. The corresponding torsion angles in **2**, **3** and **1·3** are in the range of −2.3 to 5.7°, while **1** shows angles of 21 and −164° (Table 1). Obviously, the fluorinated compounds having more than one fluorine atom per phenyl ring tend to crystallize with

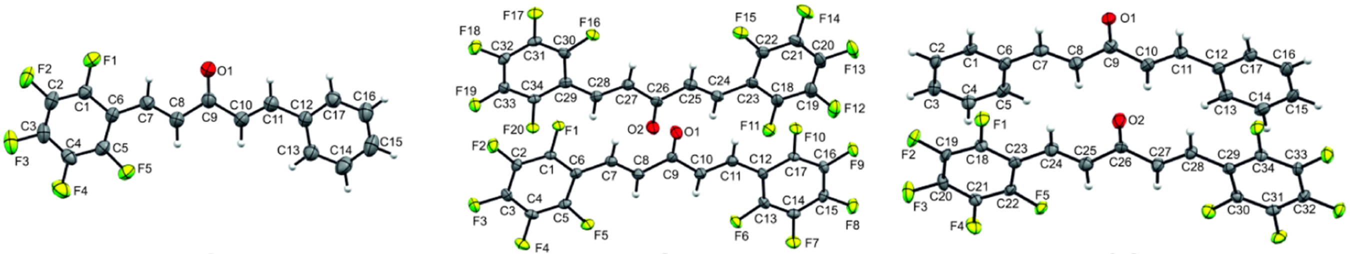


Figure 2. Perspective views of the asymmetric unit of **2**, **3**, and **1·3** in the respective crystals including atom numbering scheme. Thermal ellipsoids are at the 50% probability level.

Table 1. Torsion Angles To Describe the Rotational Isomers for Compounds 1−3 and 1·3

	atoms involved in dihedral angle	angle in deg
1[58]	O1a−C9a−C8a−C7a	21.06
	O1b−C9b−C8b−C7b	−164.82
2	C7−C8−C9−O1	−2.3(4)
	O1−C9−C10−C11	3.2(4)
3	C7−C8−C9−O1	1.6(4)
	O1−C9−C10−C11	1.0(4)
	C24−C25−C26−O2	5.7(4)
	O2−C26−C27−C28	−3.5(4)
1·3	C7−C8−C9−O1	−1.8(6)
	O1−C9−C10−C11	1.3(6)
	C24−C25−C26−O2	3.2(6)
	O2−C26−C27−C28	0.6(6)

only one isomer indicating an influence of the fluorine atoms on the molecular geometry.

Both compound **1**[58] and the *para*-fluoro disubstituted derivative mentioned above[59] are not planar with respect to the whole molecule. Due to the close similarity between the two compounds, we limit the discussion to **1**. While the molecular structure of **1** shows a maximum atomic deviation from the least-squares plane of about 0.38 Å, the components in the structures **2**, **3** and **1·3** are almost planar with deviations of only 0.06−0.10 Å. The mean planes of the phenyl rings in compound **1** form dihedral angles of about 52° but show an average angle of only 4.8° in **2**, **3** and the co-crystal **1·3**. The angles between the mean plane of the phenyl moiety and the penta-1,4-dien-3-one unit are 10.91° in average for all unsubstituted phenyl rings and 4.56° in average for all pentafluoro substituted rings regarding **2**, **3**, and **1·3**. In compound **1** the corresponding angle is about 30°. Moreover, it has to be considered that the penta-1,4-dien-3-one unit is not planar in **1**, while in **2**, **3**, and **1·3** this moiety shows an average of the r.m.s. of 0.0196. Hence, it is obvious that the fluorine substituents exert a distinct influence on the molecular geometry. In summary, the molecular structure of **1** crystallizing as single molecule cannot be described as planar but is forced to adopt a planar geometry in the 1:1 co-crystal with the decafluorinated compound **3**. In addition, **2** and **3** exhibit an almost complete planar molecular geometry. This indicates that the molecular arrangement and planarity in detail is influenced distinctly by the number of fluorine atoms bonded to the aromatic ring.

Table 2. Geometrical Parameters for Intermolecular C−H···O-, C−H···F, and C−F···Ar^F Contacts in Compounds 1−3 and 1·3[a]

	interaction	symmetry	*d*(X···A) in Å	*d*(C···A) in Å	*θ*(C−X···A) in deg
1[58]	C2A−H2A···Cg1[b]	*x*, −1 − *y*, −1/2 + *z*	3.176	3.717	119
2	C11−H11···O1	1 − *x*, −1 − *y*, −*z*	2.52	3.420(3)	159
	C17−H17···O1	1 − *x*, −1 − *y*, −*z*	2.68	3.531(3)	149
	C14−H14···F2	*x*, 1/2 − *y*, −1/2 + *z*	2.58	3.526(3)	176
	C10−H10···F4	−*x*, 1 − *y*, −*z*	2.48	3.422(3)	174
	C13−H13···F4	−*x*, 1 − *y*, −*z*	2.64	3.544(3)	159
3	C11−H11···O2	−1 + *x*, *y*, *z*	2.63	3.566(3)	170
	C28−H28···O1	1 + *x*, *y*, *z*	2.65	3.590(3)	169
	C24−H24···F10	1 + *x*, *y*, *z*	2.52	3.454(3)	168
	C7−H7···F20	−1 + *x*, *y*, *z*	2.54	3.474(3)	169
	C27−H27···F8	*x*, 1/2 − *y*, −1/2 + *z*	2.67	3.553(3)	156
	C2−F2···Cg4[b]	2 − *x*, −1/2 + *y*, 3/2 − *z*	3.546(2)	4.798(3)	155
	C32−F18···Cg4[b]	2 − *x*, −1/2 + *y*, 3/2 − *z*	3.634(3)	4.486(3)	122
	C15−F8···*π*(C27−C28)[c]	−1 + *x*, 1/2 − *y*, 1/2 + *z*	3.015(3)	4.225(4)	150
	C1−F1···Cg5[b]	*x*, *y*, *z*	3.2198(19)	3.710(3)	101
	C3−F3···Cg3[b]	2 − *x*, 1 − *y*, 1 − *z*	3.4333(19)	3.694(3)	90
	C13−F6···Cg2[b]	2 − *x*, 1 − *y*, 1 − *z*	3.3179(19)	3.662(3)	94
	C17−F10···Cg4[b]	*x*, *y*, *z*	3.365(2)	3.762(3)	96
	C18−F11···Cg3[b]	*x*, *y*, *z*	3.2126(19)	3.698(3)	100
	C19−F12···Cg5[b]	−1 + *x*, 1/2 − *y*, 1/2 + *z*	3.371(2)	4.593(3)	151
	C34−F20···Cg2[b]	*x*, *y*, *z*	3.3401(19)	3.768(3)	98
1·3	C28−H28···O2	1 − *x*, 2 − *y*, 1 − *z*	2.44	3.363(5)	165
	C11−H11···O1	2 − *x*, 2 − *y*, 1 − *z*	2.53	3.428(5)	158
	C8−H8···F7	1 − *x*, 1 − *y*, 1 − *z*	2.41	3.339(4)	166
	C24−H24···F10	1 − *x*, 2 − *y*, −*z*	2.49	3.399(5)	161
	C1−H1···F2	2 − *x*, 2 − *y*, −*z*	2.60	3.250(4)	126
	C3−H3···F8	1 + *x*, *y*, −1 + *z*	2.65	3.573(4)	165
	C3−H3···F9	1 + *x*, *y*, −1 + *z*	2.65	3.320(4)	128
	C18−F1···Cg2	1 − *x*,1 − *y*, 1 − *z*	3.771(3)	3.479(4)	67
	C19−F2···Cg2	1 − *x*, 1 − *y*, 1 − *z*	3.784(3)	3.488(4)	67
	C21−F4···Cg2	−*x*, 1 − *y*, 1 − *z*	3.640(3)	3.420(4)	70
	C31−F7···Cg3	−*x*,1 − *y*, 1 − *z*	3.598(3)	3.355(4)	69
	C34−F10···Cg3	1 − *x*, 1 − *y*, 1 − *z*	3.638(3)	3.462(4)	72

[a] *d*(C−H) = 0.95 Å; X is the interacting atom, A is the acceptor. All angles are rounded off. [b] Cg is defined as the centroid of the rings (center of gravity): Cg1: C1A−C6A; Cg2: C1−C6, Cg3: C12−C17; Cg4: C18−C23; Cg5: C29−C34. [c] Geometric parameter are given for C15−F8···C28.

Table 3. Geometrical Parameters for Intermolecular Ar···Ar^F Interactions in Compounds 2 and 1·3

	symmetry code	CgI[a]	CgJ[a]	CgI···CgJ/Å	CgI···P(J)[b]/Å	CgJ···P(I)[c]/Å
2	$1 - x, -y, -z$	Cg2	Cg3	4.0255(16)	3.5444(11)	3.4208(12)
	$2 - x, -y, -z$	Cg2	Cg3	3.8088(16)	3.5029(11)	3.3874(12)
1·3	$-x, 1 - y, 1 - z$	Cg4	Cg2	3.736(2)	3.4681(16)	3.3939(16)
	$1 - x, 1 - y, 1 - z$	Cg4	Cg2	3.693(2)	3.4928(16)	3.4054(16)
	$-x, 1 - y, 1 - z$	Cg5	Cg3	3.641(2)	3.3879(15)	3.3459(16)
	$1 - x, 1 - y, 1 - z$	Cg5	Cg3	3.791(2)	3.4471(15)	3.4075(16)

[a] Cg is defined as the centroid of the rings (center of gravity): Cg2: C1−C6, Cg3: C12−C17; Cg4: C18−C23; Cg5: C29−C34. [b] Perpendicular distance of the centroid CgI on ring plane J. [c] Perpendicular distance of the centroid CgJ on ring plane I.

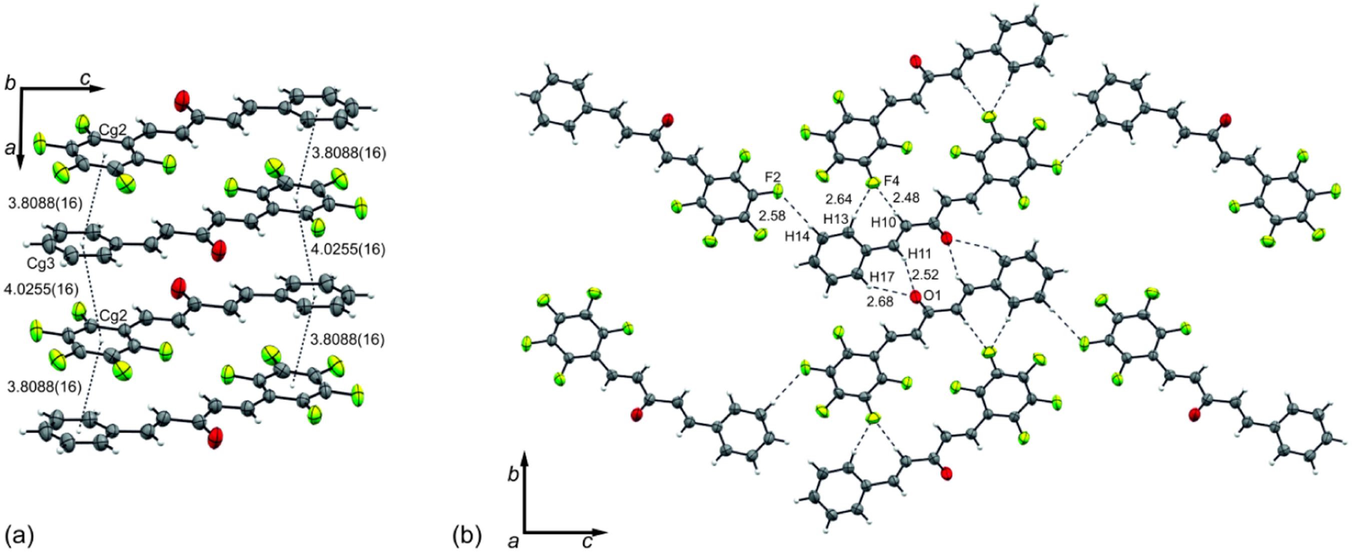


Figure 3. Views of the crystalline packing of **2**: (a) along the *b* axis showing the shortest distances (Å) between the centroids of adjacent stacks; (b) along the *a* axis giving rise to the C−H···O and C−H···F contacts of one selected layer. Noncovalent contacts are represented as broken lines.

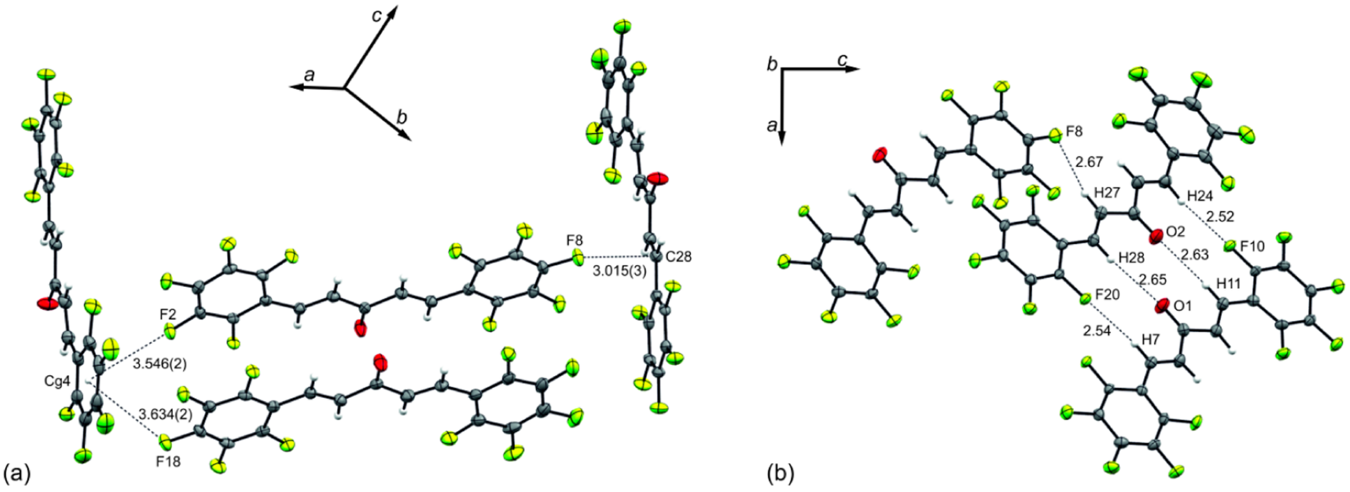


Figure 4. Crystalline packing of **3**: (a) showing relevant intermolecular C−F···Ar contacts; (b) along the *b* axis giving rise to relevant C−H···O and C−H···F interactions. Noncovalent contacts are represented as broken lines.

Apart from the molecular features, the crystalline state is influenced by the molecular arrangement and the interaction between adjacent units. In the current study, compound **1** is the only one not bearing a fluorine atom potentially competing with the carbonyl oxygen atom.[58] Unlike the expectation, the carbonylic oxygen atom is not involved in any interaction. However, C−H···π contacts form zigzag chains along the crystallographic *c* axis (Table 2).

On the other hand, compound **2** bearing a phenyl and a pentafluorinated phenyl ring should be able to form intermolecular strands of the Ar···Ar^F type.[2,3,5] In fact, the structure of **2** features stacks of alternately arranged phenyl and pentafluorophenyl rings in an offset face-to-face orientation of adjacent aromatic rings. The perpendicular distances of the centroids of the interacting ring planes, as specified in Table 3 and given in Figure 3a, are 3.8 and 4.0 Å. While the latter

Table 4. Geometrical Parameters for Intermolecular C−F⋯F Contacts in Compounds 2, 3, and 1·3[a]

	interaction	symmetry	C−F/Å	F⋯F/Å	C−F⋯F/deg	Type
2	C5−F5⋯F5−C5	−*x*, 1 − *y*, −*z*	1.340(3)	2.700(3)	169	I
	C2−F2⋯F3−C3	−*x*, −1/2 + *y*, 1/2 − *z*	1.347(3)	2.881(2)	140	II
			1.343(3)		151	
3	C5−F5⋯F5−C5	3 − *x*, −*y*, 2 − *z*	1.338(3)	2.531(3)	156	I
	C2−F2⋯F14−C21	1 − *x*, −1/2 + *y*, 1.5 − *z*	1.344(3)	2.736(2)	126	II
			1.337(3)		170	
	C4−F4⋯F6−C13	1 − *x*, 1/2 + *y*, 1.5 − *z*	1.347(3)	2.767(2)	126	II
			1.343(3)		166	
	C20−F13⋯F17−C31	−1 + *x*, 1/2 + *y*, 1.5 − *z*	1.350(3)	2.775(2)	140	II
			1.339(3)		109	
1≅3	C19−F2⋯F2−C19	1 − *x*, 2 − *y*, −*z*	1.341(4)	2.866(4)	88	I
	C21−F4⋯F4−C21	1 − *x*, 1 − *y*, − *z*	1.337(4)	2.822(4)	126	I

[a] All angles are rounded off.

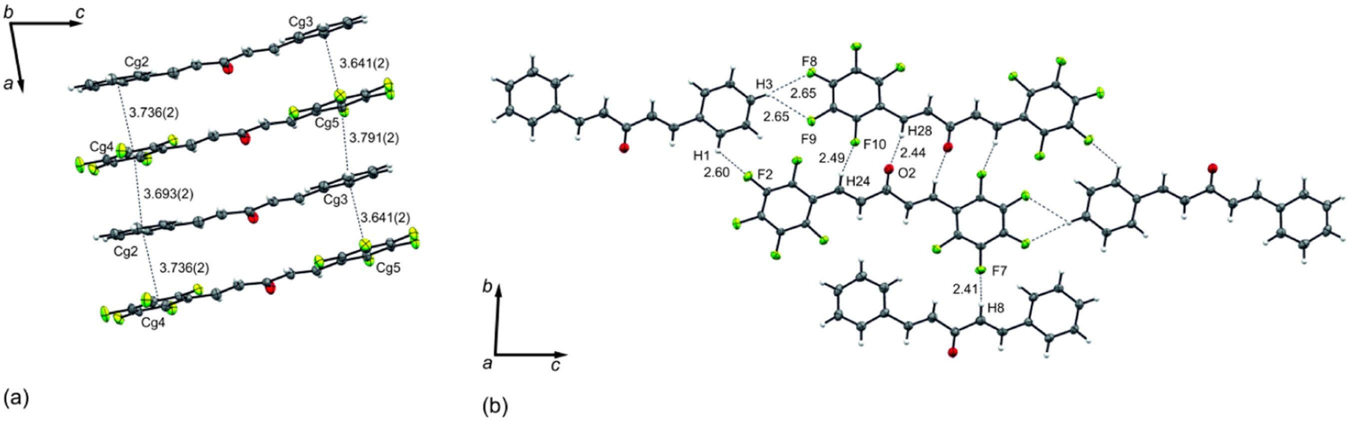


Figure 5. Crystalline packing of **1·3**: (a) along the *b* axis showing the shortest distances (Å) between the centroids of adjacent stacks; (b) along the *a* axis giving rise to relevant C−H⋯O and C−H⋯F interactions. Noncovalent contacts are represented as broken lines.

distance is quite long indicating only a weak contact, the other one is in a range suggesting a stabilizing Ar⋯Ar^F interaction. In addition, layers are formed involving C−H⋯O[61] bonded dimers (2.5−2.6 Å) that interact via C−H⋯F and F⋯F contacts resulting in a herringbone mode of supramolecular architecture [Table 2, Figure 3b]. The C−H⋯F interactions are in the range of 2.5−2.6 Å with angles of 159−176° indicating a significant impact on the molecular arrangement. In contrast, the distances between adjacent fluorine atoms are 2.700 Å (angle at *F* = 169°) and 2.881 Å (angle at *F* = 140° and 151°). However, their importance for the crystal packing seems secondary. Instead, they support stabilizing the stacks of molecules generated by the Ar⋯Ar^F interaction.

Thus, C−H⋯O and C−H⋯F interactions occur in **2** not only as connecting element between the stacks but also show a significant impact on the strength of the Ar⋯Ar^F synthon. The longer distances between the adjacent stacks indicate a weakened Ar⋯Ar^F interaction.

The crystal structure of the derivative **3**, not containing any aromatic bonded hydrogen atoms, does not feature stacking interactions. The shortest distance between adjacent ring centroids is 4.407 Å. Instead, several robust C−F⋯Ar^F contacts[31,33] are found with angles around and below 100° and some angles between 120 and 155° (Table 2) leading to domains of molecular stacks. In addition, there is a C−F⋯ *π* contact involving F(8) and the olefinic double bond as *π*-moiety[62] with a distance of 3.015 Å and an angle of 149.5°. Apart from the interactions including the aromatic units, several other contacts are found, in particular of the C−H⋯O and C−H⋯F type. As depicted in Figure 4 and Table 2, the C−H⋯O contacts with a distance of about 2.6 Å give rise to dimer formation within a layer. These layers are connected via C−H⋯F interactions in the range of 2.5−2.6 Å (Table 2). Furthermore, several fluorine atoms are located closer to each other than their sum of the van der Waals radii of 1.47 Å.[63] They show distances in the range of 2.5−2.8 Å with angles of 109−170° (Table 4). While in **2** types I and II of halogen−halogen interaction[3] occur, the decafluorinated derivative **3** seems to prefer type II. These contacts connect the domains of stacks generated by the C−F⋯*π*^{F} interaction.

Hence, the C−F⋯Ar^F contact seems to be the interaction with the greatest impact on the crystal structure of compound **3**, similar to the C−H⋯*π* interaction in compound **1**. But in **3** additional C−H⋯O and C−H⋯F interactions are found. This suggests a weaker influence of the C−F⋯Ar^F contacts on a crystal structure than C−H⋯*π* in **1** since here the carbonyl group is not involved in intermolecular interactions.

The co-crystals between compounds **1** and **3**, **1·3**, generated via crystallization of the components in a 1:1 ratio from chloroform crystallizes in the triclinic space group *P*1̄ with two independent molecules in the asymmetric unit. As mentioned above, the molecular structure features planarity and shows no disorder or isomerism. In keeping with the expectation, the molecular arrangement in the crystal structure is mainly determined by an Ar⋯Ar^F stacking motif (Table 3). The resulting strands with distances between adjacent molecules of

3.6–3.8 Å are illustrated in Figure 5a. The slippage of the phenyl moieties indicates an offset face-to-face orientation. Figure 5b shows one layer generated by the connection between several stacks being realized by C–H···O and C–H···F interactions in the range of 2.4–2.6 Å (Table 2). Furthermore, the distances between fluorine and the center of adjacent pentafluorophenyl rings ranging between 3.6 and 3.8 Å suggest C–F···Ar^F interactions (Table 3). Nevertheless, the contact angles are below 72° and therefore indicate no significance. Table 4 gives the geometric parameters of located type I C–F···F contacts with distances of about 2.8 Å and angles of 88° and 126°. These contacts assist in connecting the decafluorinated molecules of adjacent stacks.

In the crystal structure of the co-crystal **1·3** a similar interplay of the respective interactions is found as in **2**. However, the significance of the Ar···Ar^F interaction is more important in **1·3** indicated by the distances of the aromatic moieties.

CONCLUSION

Three different dibenzalacetones including the fluorine-free parent compound and the pentafluoro- and the decafluoro substituted derivatives have been prepared. They were studied regarding their capacity to form a $\pi\cdots\pi^F$ stacking motif in the crystalline state competing with or supported by other types of possible noncovalent interactions, allowing for the potential generation of co-crystals among one another. Considering the raised questions and based on the results, conclusions can be drawn as follows.

The mode of fluorine substitution exerts a distinct influence on the geometry of the dibenzalacetone moiety in this compound system in that a certain number of fluorine substituents is required to prevent molecular disorder and promote planarity of the molecule. If possible and in competition with other types of noncovalent interactions, the particular Ar···Ar^F stacking interaction is found in the crystal structures of **2** and also of the co-crystal **1·3**. With reference to the C–H···π, C–H···O, C–H···F, C–F···Ar^F, and F···F type of interactions, reflections regarding interdependency and dominance are difficult to make. However, considering the current and including the structures of di- and tetrafluoro derivatives,[59,60] it is apparent that the carbonyl oxygen atom starts interaction to hydrogen atoms as soon as fluorine is present in the molecule. Moreover, in **2** the C–H···O and C–H···F contacts are more important than in **1·3** at the expense of the Ar···Ar^F interaction. And finally, analogous to previous findings,[21,25] one gets the impression that Ar···Ar^F stacking generated from phenyl and pentafluorophenyl moieties is also essential to a successful co-crystallization between individuals of this class of compounds. But this comes into conflict with the experimental results concerning co-crystallization of **2** with either **1** or **3**. In these cases, we were unable to isolate respective co-crystals, although the Ar···Ar^F contact is a typical interaction mode in the crystal structure of pure **2**. One may conclude that in these latter cases the energetic differences of each possible crystal phase are small preventing experimental isolation.

In summary, it is shown in this study that dependent on certain structural conditions, the dibenzalacetone framework is suitable for co-crystal formation.

ASSOCIATED CONTENT

Supporting Information

Crystallographic information file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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DEDICATION

This paper is dedicated to Dr. Wilhelm Seichter on the occasion of his 65th birthday.

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(55) Crystal data for **1·3**: $C_{17}H_4F_{10}O\cdot C_{17}H_{14}O$, M = 648.48, triclinic, a = 7.4146(12) Å, b = 11.1034(17) Å, c = 17.304(3) Å, α = 86.917(8)°, β = 79.945(8)°, γ = 74.085(8)°, V = 1348.9(4) Å^3, T = 93(2) K, space group $P\bar{1}$, Z = 2, μ(Mo Kα) = 0.146 mm^{-1}, 28 298 reflections measured, 4865 independent reflections (R_{int} = 0.0673). The final R_1 values were 0.0700 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1687 ($I > 2\sigma(I)$). The final R_1 values were 0.1121 (all data). The final $wR(F^2)$ values were 0.1864 (all data). The goodness of fit on F^2 was 1.046. CCDC no. 742630. Crystal data for **2**: $C_{17}H_9F_5O$, M = 324.24, monoclinic, a = 7.6428(4) Å, b = 6.1654(3) Å, c = 29.1997(16) Å, β = 91.079(2)°, V = 1375.67(12) Å^3, T = 173(2) K, space group $P2_1/c$, Z = 4, μ(Mo Kα) = 0.143 mm^{-1}, 12 809 reflections measured, 1917 independent reflections (R_{int} = 0.0316). The final R_1 values were 0.0428 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1086 ($I > 2\sigma(I)$). The final R_1 values were 0.0550 (all data). The final $wR(F^2)$ values were 0.1175 (all data). The goodness of fit on F^2 was 1.058. CCDC no. 742633. Crystal data for **3**: $C_{17}H_4F_{10}O$, M = 414.20, monoclinic, a = 5.6259(8) Å, b = 24.346(4) Å, c = 21.186(3) Å, β = 90.348(5)°, V = 2901.8(7) Å^3, T = 93(2) K, space group $P2_1/c$, Z = 8, μ(MoKα) = 0.206 mm^{-1}, 33 777 reflections measured, 5246 independent reflections (R_{int} = 0.0376). The final R_1 values were 0.0457 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1203 ($I > 2\sigma(I)$). The final R_1 values were 0.0622 (all data). The final $wR(F^2)$ values were 0.1281 (all data). The goodness of fit on F^2 was 1.090. CCDC no. 742634.

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