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Involvement of organic fluorine substitution in the crystalline packing structures of tricyclic Diels–Alder adducts derived from diarylfulvenes and *N*-arylimides

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ABSTRACT

Fluorinated tricyclic Diels–Alder adducts derived from corresponding diarylfulvenes and *N*-arylmaleimides, each of different degree and positions of the fluorine substituents, and including the non-fluorinated parent compound, have been synthesized. Their X-ray crystal structures were determined in order to study the effect of fluorine substitution on the solid state organization in competition with other weak intermolecular interactions. A balanced interplay of C–H···O, C–H···F and especially C–H···π contacts is typical of the crystal packings while other potential interactions such as C–F···F, C–F···π^F, π^H···π^F and Br···Br are secondary or not to be found. Isostructurality calculations and comparison of molecular conformations have been performed in order to structurally classify the compounds depending on the number and mode of fluorination.

1. Introduction

Crystal engineering via the manipulation of intramolecular interactions has become a major area of research in recent years [1]. In the course of these studies, different types of packing motifs in crystals including bonding potentials such as strong (O–H···O, O–H···N, N–H···O, N–H···N) [2] and weaker (C–H···O, C–H···π) [3,4] hydrogen bonding or π-stacking interactions [5] have been discussed in detail. Having a more profound understanding of the nature and strength of organic fluorine involved non-covalent interactions is another current challenge [6]. A motive for it is that fluorinated organic compounds often show particular physical and chemical behaviour [7] that can be utilized in pharmaceutics [8] and materials science [9]. Replacement of hydrogen by fluorine in organic molecules was also found to lead to distinct changes in between crystal structure [10] or turned to good account in solid state reactions [11] and crystalline inclusion chemistry [12]. As a result, crystal engineering of fluoroorganic compounds has become a very actual topic [13].

Within this frame, specific modes of organic fluorine involving weak interactions are considered to be rather effective, first and foremost applying to the Ar···Ar^F staking motif [5,14], while others are rated less distinct in their effectiveness (C–F···H, C–F···F and C–F···π^F) [15–18] thus causing sometimes a questioning of their existence [6,10,19]. However, a particular problem arises if further non-dominating interactions including weaker hydrogen bonds (O–H···π, C–H···π) [3,4] or X···X contacts between the higher halogens [20] compete. This has prompted to systematically study the crystal structures of properly fluorinated organic compounds [10]. A new such testing system of fluoroorganic compounds is provided with the present series of Diels–Alder adducts **1**–**18** (Scheme 1). Compared to the previously studied groups of fluorinated *N*-phenylmaleimides and corresponding phthalimides of different fluorine substitution [21], the tricyclic fulvene with arylimide Diels–Alder adducts, discussed here, are more rigid and bulky molecules containing additional aromatic rings.

2. Results and discussion

2.1. Compounds studied

The compounds studied in this paper involve a systematic series of fluorinated molecules **1**–**18** (Scheme 1) that feature a tricyclic framework of *N*-arylimides. Compound **1** is the non-fluorinated parent molecule. The compounds **2**–**6** represent derivatives with different number and positions of fluorine atoms substituted into the *N*-phenyl unit. In **7**–**12**, the organic fluorine substituents are included both in the *N*-phenyl unit and *p*-positioned in the two phenyl rings attached to the methylidene group. Hence the fluorine substituents are found either on one or both sides of the molecule. Compounds **13**–**18** differ from **7** to **12** in the replacement of the fluorine substituents of the methylidene

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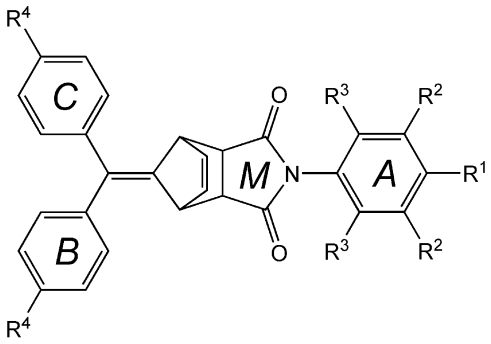
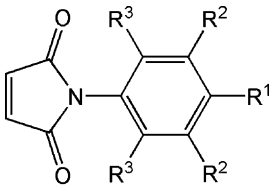
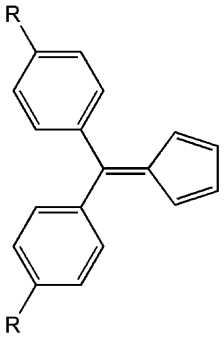


	R^1	R^2	R^3	R^4
1	H	H	H	H
2	F	H	H	H
3	H	F	H	H
4	H	H	F	H
5	F	H	F	H
6	F	F	F	H
7	H	H	H	F
8	F	H	H	F
9	H	F	H	F
10	H	H	F	F
11	F	H	F	F
12	F	F	F	F
13	H	H	H	Br
14	F	H	H	Br
15	H	F	H	Br
16	H	H	F	Br
17	F	H	F	Br
18	F	F	F	Br

Scheme 1. Formula structures of compounds studied with designation of ring planes.



	R^1	R^2	R^3
19a	H	H	H
b	F	H	H
c	H	F	H
d	H	H	F
e	F	H	F
f	F	F	F



20a R = H
b R = F
c R = Br

Scheme 2. Formula structures of imide and fulvene intermediates.

bound phenyl rings for bromine atoms. This opens the possibility to explore the effect of bromine versus fluorine in the formation of the crystal packing.

All the compounds **1**–**18** have been synthesized via Diels–Alder reactions [22] using the respective *N*-arylimides **19a**–**f** and the corresponding diarylfulvenes **20a**–**c** (Scheme 2). They are colourless solids that show high temperature melting points (>200 °C) attended by decomposition. There is no report in the literature with reference to these compounds, except for **1** giving, however, a melting point that has not been approved [23]. The *N*-arylimides **19a**–**f** were prepared from condensation reaction [24] of maleic anhydride and the respective aniline [21], the fulvenes **20a**–**c** [25] from corresponding diaryl ketones and 1,3-cyclopentadiene [26].

All the compounds being 2,6-difluoro substituted in the *N*-phenyl unit (**4**–**6**, **10**–**12** and **16**–**18**) show a hindered conformational rotation around the *N*-aryl bond at $T = 26$ °C. This has been proven by ^{19}F NMR determination in $CDCl_3$, giving rise to separate signals for the 2- and 6-fluoro substituents (see Section 4). The potential energy of the rotational barrier was calculated to be in the range of 100 kJ/mol with the minimum of the potential energy at an interplanar angle relating to the pyrrolidine and the aryl ring of about 60°. DFT calculations on **19d** have been performed at the B3LYP/6-311G(d) level of theory using GAUSSIAN 03 [27].

In order to probe the capacity of solvent inclusion [28], the target compounds **1**–**18** were recrystallized from a wide range of polar and apolar solvents including methanol, ethanol, *n*-butanol, diethylamine, triethylamine, acetone, butanone, ethyl acetate, dimethylformamide, dimethylsulfoxide, dichloromethane, chloroform, tetrachloromethane, benzene, toluene, xylenes, and mesitylene. Only in the case of **14** and benzene, a respective 1:1 crystalline solvent inclusion compound **14**·C_6H_6 was obtained. All other compounds failed to form solvent inclusions. This suggests almost non-existent clathrate behaviour of this compound family, though potential molecular bulkiness is present, which has been defined a favourable parameter of clathrate formation [28,29]. Apparently, with the exception of **14**, the molecules offer good opportunity to pack in a crystal lattice without making use of solvent assistance.

Aside from **15** and **16**, single crystals of the target compounds suitable for X-ray structure analysis were obtained by isothermal evaporation or cooling of a saturated solution from acetone or benzene. Their crystal structures are comparatively discussed in the following. Dependent on the mode of fluorine substitution, a subdivision is made into different categories of compounds including the non-fluorinated parent molecule **1**, compounds with the fluorine atoms attached to the *N*-phenyl unit (**2**–**6**), compounds possessing fluorine atoms in the methylidene bound phenyl rings (**7**–**12**) and compounds containing additional bromo substituents (**13**, **14**·C_6H_6, **17**, **18**).

2.2. X-ray single crystal structures

The crystallographic data and structure refinement parameters for the studied compounds (**1**–**13**, **14**·C_6H_6, **17** and **18**) are

Table 1
Selected geometric features of compounds **1**–**13**, **14**·C_6H_6, **17** and **18**[a].

	1	**2**	**3**	**4**	**5**	**6-1**	**6-2**
2′- and 6′-substitution	H	H	H	F	F	F	F
M–A interplanar angle (°)	74.79	82.45	75.81	68.81	76.48	75.93	65.12
B–C interplanar angle (°)	87.39	81.03	85.51	87.73	81.02	77.56	78.61
M–B interplanar angle (°)	66.86	49.85	45.27	72.71	51.28	53.30	66.42
M–C interplanar angle (°)	47.66	54.04	72.30	44.69	51.73	54.32	41.93
N–C(=O) (Å)	1.4007	1.389	1.404	1.4037	1.4017	1.411	1.414
	1.4013	1.398	1.405	1.4039	1.4031	1.413	1.445
C_{Aryl}–N (Å)	1.441	1.442	1.442	1.423	1.424	1.413	1.445

	7	**8**	**9**	**10**	**11**	**12**
2′- and 6′-substitution	H	H	H	F	F	F
M–A interplanar angle (°)	81.53	81.91	69.85	66.70	76.55	61.31
B–C interplanar angle (°)	83.00	81.55	83.73	88.33	82.41	75.32
M–B interplanar angle (°)	52.11	50.58	43.07	71.36	51.25	63.21
M–C interplanar angle (°)	59.89	60.89	69.68	42.51	63.98	46.72
N–C(=O) (Å)	1.3889	1.390	1.392	1.402	1.4017	1.413
	1.3925	1.390	1.412	1.408	1.4031	1.419
C_{Aryl}–N (Å)	1.434	1.430	1.432	1.425	1.425	1.421

	13	**14**·C_6H_6	**17**	**18**
2′- and 6′-substitution	H	H	F	F
M–A interplanar angle (°)	77.28	51.36	80.85	81.22
B–C interplanar angle (°)	73.59	60.25	75.10	72.53
M–B interplanar angle (°)	49.60	43.06	56.91	54.69
M–C interplanar angle (°)	61.09	46.16	47.33	51.85
N–C(=O) (Å)	1.393	1.400	1.401	1.405
	1.393	1.412	1.403	1.414
C_{Aryl}–N (Å)	1.436	1.436	1.423	1.414

[a] Designation of the ring mean planes in Scheme 1.

summarized in Table S1 (SI). For the description of the crystal structures, intermolecular contacts within the sum of the van-der-Waals radii [30] for the pair of interacting atoms (O···H, F···H and F···F) and an angular cut off of >110 °C have been used. Contacts between the aryl units and the hydrogen or fluorine atoms are based upon the centre of the ring. Selected geometric features of the structures are presented in Table 1. Weak intermolecular hydrogen bond type (C–H···O, C–H···F, C–H···π/π^F) as well as C–F···F and C–Br···O contacts are represented in Tables S2–S4 (SI), respectively.

2.2.1. Non-fluorinated parent compound **1**

The non-fluorinated parent compound **1** was found to crystallize in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. Due to intramolecular steric repulsion, the imide ring shows a distortion of 74° relative to the phenyl unit, referring to non-existent conjugation between these two moieties (Fig. 1). The crystal packing of compound **1** is dominated by C–H···π interactions [4] with distances that range between 2.77 and 2.98 Å, creating intermolecular zigzag chains or dimers. Only one C–H···O contact (C15–H15···O1: 2.32 Å, 163.8°) is present, giving rise to intermolecular dimer formation (Fig. 2).

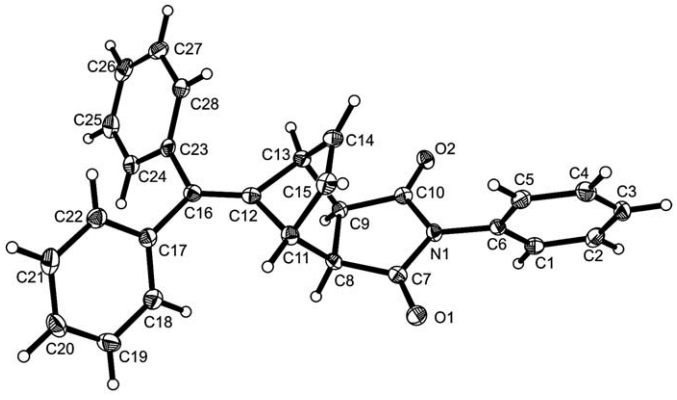


Fig. 1. ORTEP-Plot of compound **1** including atom numbering scheme. Thermal ellipsoids are at the 50% probability level, respectively.

*2.2.2. Compounds fluorinated at the N-phenyl ring subunit (***2**–**6**)

The molecular structures of compounds **2**–**6** are comparable to the parent molecule **1**, showing also a distortion around the N–C_{aryl} bond to yield interplanar angles between the imide and *N*-aryl rings that range from 65° to 82°. However, a clear relation between the interplanar angles and the mode of fluorine substitution is not becoming evident. A similar situation is revealed for the N–C(=O) bond lengths. On the other hand, an observed shortening of the N–C_{aryl} bond length in the compounds **4**–**6** seems to be correlated with the fluorine substitution in the 2- and 6-positions of the aryl ring (Fig. 3).

In the crystalline packings of compounds **2**–**6**, C–H···O contacts [3] mainly including aliphatic and olefinic hydrogen atoms are rather frequent. On the other hand, it is a reasonable consequence that with increasing fluorine substitution in the molecule, the intermolecular C–H···F contacts [13] also increase. But these C–H···F contacts are rather weak and thus their impact on the crystal structure is in question. Only in compounds **4** and **6**, these contacts seem to be of more significance due to a shortened distance between the interacting atoms. In the 3,5-difluorinated derivative **4**, the contact C11–H11···F1 (2.46 Å, 121.0°) is involved in the formation of molecular zigzag chains along the crystallographic *b*-axis which, however, are possibly more a result of the higher effectiveness of the C–H···O interaction (C8–H8···O1: 2.49 Å, 116.7°). By the way of contrast, the C55–H55···F4 (2.49 Å, 132.1°) and C27–H27···F7 (2.44 Å, 139.9°) contacts form dimers in the crystal structure of the pentafluorinated compound **6**, giving rise to an intermolecular zigzag chain in the combination.

Interestingly, in all compounds **2**–**6** only one single fluorine–fluorine contact is found, if at all, since this contact is a rather weak

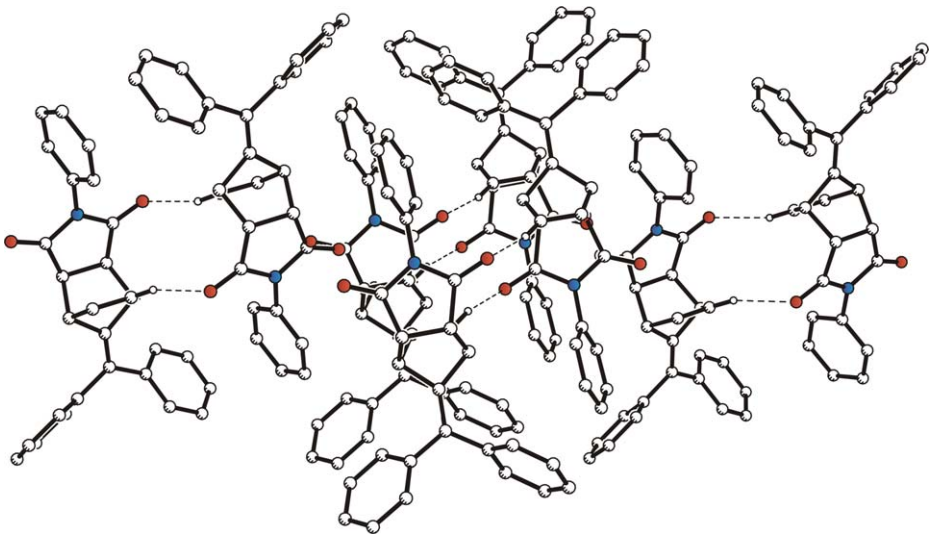


Fig. 2. Packing diagram of **1** along the crystallographic *c*-axis. Heteroatoms are shaded. The C–H···O contacts are shown as broken lines. Non-relevant hydrogen atoms are omitted for clarity.

one (C2–F2···F6–C29: 2.81 Å, 173.0° and 145.7°), and might perhaps merely be a result of the interplay of more effective interactions in the crystal packing. Moreover, in **6** a potential aryl-perfluoroaryl interaction [13] is found in the asymmetric unit. However, considering the centre-to-centre distance of 3.9 Å and the angle of 21.1° between the aryl planes, the presence of a respective stacking motif is rather questionable. In the compounds **2**–**5**, the centre-to-centre-distances of 4.2–5.7 Å between aryl-fluoroaryl units are far beyond being of any significance to the packing structure.

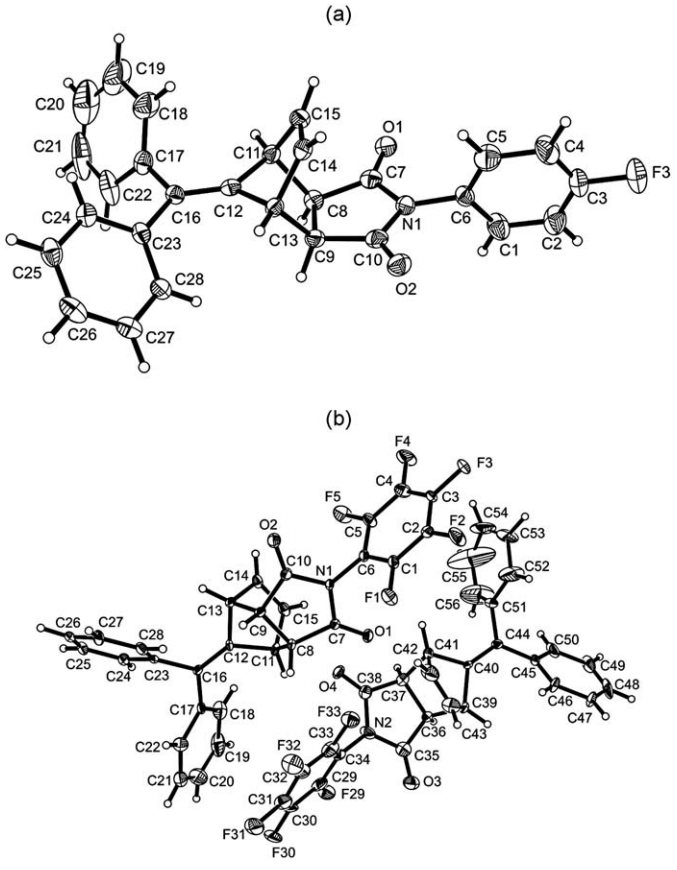


Fig. 3. ORTEP-Plots of compounds **2** (a) and **6** (b) including atom numbering scheme. Thermal ellipsoids are at the 50% probability level, respectively.

On the other side, in the compounds **2**–**6**, contacts of the C–H···π type [4] are more essential to the packing structures, although in **2** only one rather weak contact with a hydrogen-centre distance of 3.2 Å is present. But in **3**–**6**, the corresponding distances ranging from 2.7 to 2.9 Å point to higher effectiveness. These contacts result in the formation of intermolecular zigzag chains of molecules along the crystallographic *b*-axis. Logically, with an increasing number of fluorine substituents in the phenyl unit, the number of C–H···π contacts decreases, while their geometric parameters remain constant.

2.2.3. Compounds fluorinated on the methylidene bound phenyl groups (7–12)

Substitution of the hydrogen atoms at the *para*-position of the methylidene bound phenyl groups for fluorine atoms results in an electron withdrawing effect on these phenyl rings and may thus lead to a molecular system with electron withdrawing units at both ends of the molecule. Nevertheless, this seems to be of no relevance for the used crystal system, since no significant differences between the compounds **7**–**12** and **1**–**6** are found in this respect. They all crystallize in the monoclinic crystal system with one molecule in the asymmetric unit. More strictly speaking, except **9** which crystallizes in the space group $P2_1$, the other compounds show the space group $P2_1/c$ ($P2_1/n$). Moreover, corresponding molecular structures of the compounds **7**–**12** (examples in Fig. 4) and **1**–**6** are almost the same. This includes the interplanar angles between imide and *N*-aryl rings (range of 61–81°) as well as the non-existing dependence between N–C(=O) bond lengths and fluorine substitution. Also the N–C_{aryl} bond lengths are shortened in the cases of the 2,6-difluoro substituted compounds **10**–**12** due to reduced electron density and the resulting compensation of the charge distribution by the nitrogen atom.

With regard to the crystalline packing structures of **7**–**12**, it is shown that the oxygen involved contacts outnumber the fluorine contacts, similar to the behaviour which is found for the compounds **2**–**6**. This is even the case for the derivatives **11** and **12** being enriched with fluorine substituents. Remarkably, the compounds **9** and **12**, featuring fluorine atoms in the 3,5-position of the *N*-aryl ring, give rise to both the shortest (i.e. 2.43 Å, 146.9° for **9** and 2.40 Å, 165.3° for **12**) and longest C–H···O contacts [3]

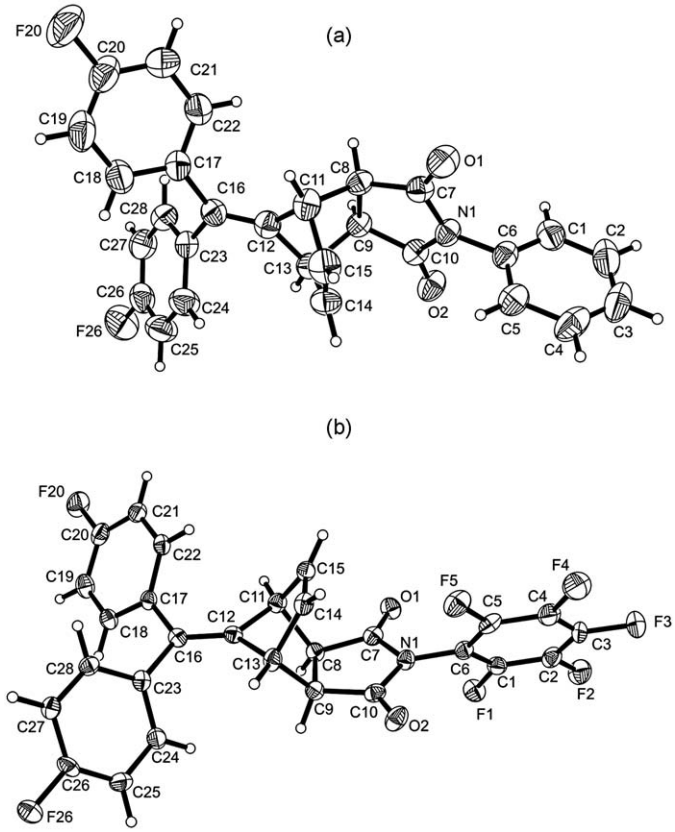


Fig. 4. ORTEP-Plots of compounds **7** (a) and **12** (b) including atom numbering scheme. Thermal ellipsoids are at the 50% probability level, respectively.

(2.71 Å, 147.2° and 2.58 Å, 131.9° for **9** and **12**, respectively) observed in this category of compounds. While these shortest contacts create chains and zigzag chains along the crystallographic *b*-axis, the long contacts lead mainly to chains and dimers. Moreover, the findings suggest that the affinity to create dimers via C–H···O contacts decreases with increasing number of fluorine atoms at the *N*-aryl ring. Therefore, dimers produced by strong C–H···O contacts can only be found in the cases of compounds **7**, **8** and **10**. As regards the derivatives **7** and **8**, a combination of weak C–H···O and C–H···F contacts induces the formation of zigzag chains along the crystallographic *b*-axis. On the other hand, in the structures of **9**, **11** and **12**, the C–H···O interactions cause intermolecular chains as well as zigzag chains.

Considering the observed range of distances (2.41–2.66 Å) for the C–H···F contacts, this type of interaction seems not to be of high relevance to the crystal structures. Possibly more important F···F contacts were only detected for compound **12** with distances 2.87 Å (107.7° and 131.6°) and 2.93 Å (80.2° and 158.1°) being slightly shorter than the sum of the van-der-Waals radii (F: 1.47 Å [30]).

2.2.4. Bromo substituted compounds (13, 14·C_6H_6, 17 and 18)

As a preliminary note, these bromine substituted compounds tend to give only crystals of moderate to poor quality. For this reason, we were unable to study the crystal structures of the difluorinated derivatives **15** and **16**. Another general finding observed for this series of compounds is the change from the primitive to face-centred lattice with the increasing number of fluorine atoms in the molecule. While the non-fluorinated compound **13** crystallizes in the space group $P2_1/c$ and the benzene solvate of **14** (**14**·C_6H_6) in $P2_1/n$, the trifluorinated derivative **17** is found to crystallize in the centrosymmetric space

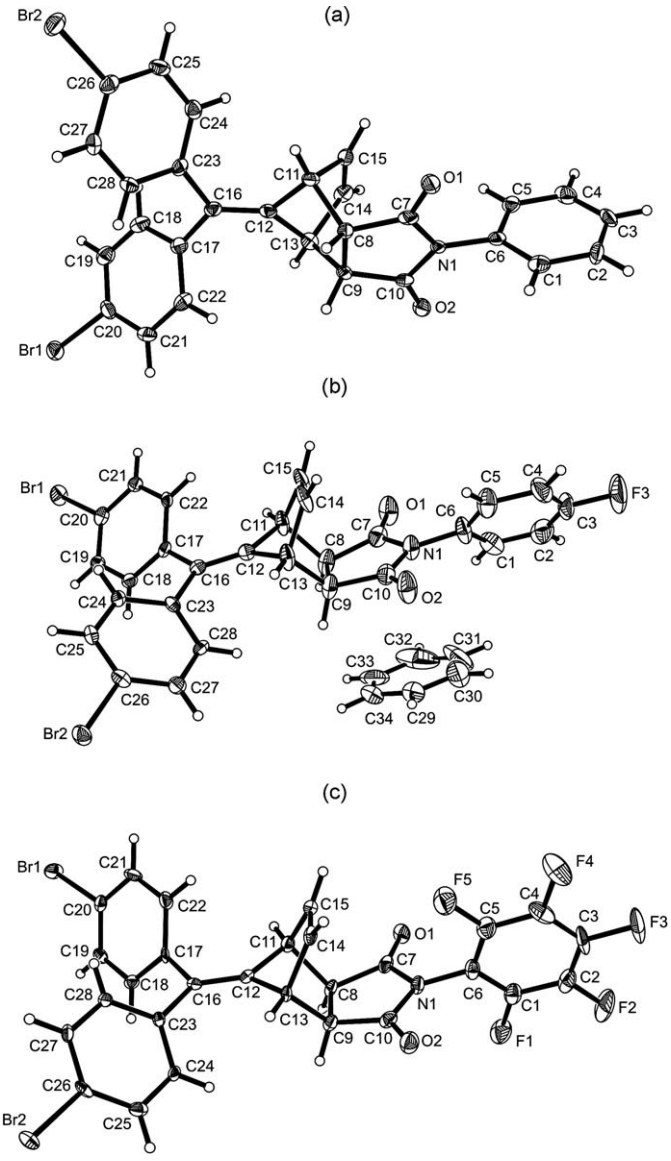


Fig. 5. ORTEP-Plots of compounds **13** (a), **14**·C_6H_6 (b) and **18** (c) including atom numbering scheme. Thermal ellipsoids are at 50% probability level, respectively.

group *C*2/*c*, and the pentafluorinated compound **18** makes use of the non-centrosymmetric space group *C*2.

The molecular geometries of the compounds **13**, **14**, **17** and **18** (examples in Fig. 5) are closely comparable to the corresponding analogous compounds with (**1**, **2**, **5**, and **6**) and without (**7**, **8**, **11**, and **12**) fluorine substitution of the *N*-phenyl ring, showing little influencing control of the bromine atoms. In the structures of the bromine substituted compounds, the interplanar angles between imide and aryl rings range from 51° to 81° (average 73°). The smallest angle was observed for **14** in the corresponding benzene solvate. As before, no interdependence involving either the interplanar angle or the N–C(=O) bond length and the mode of fluorine substitution is obvious. Moreover, in the case of the 2,6-difluoro substituted derivatives **17** and **18** the N–C_{aryl} bond lengths are shortened, which is also a property similar to the bromine-free analogues.

Among all compounds studied here, the bromofluoro derivative **14** is the only one which crystallized as a stoichiometric 1:1 solvate (host–guest inclusion compound) with benzene. The packing structure of **14**·C_6H_6 shows a remarkable feature by the formation

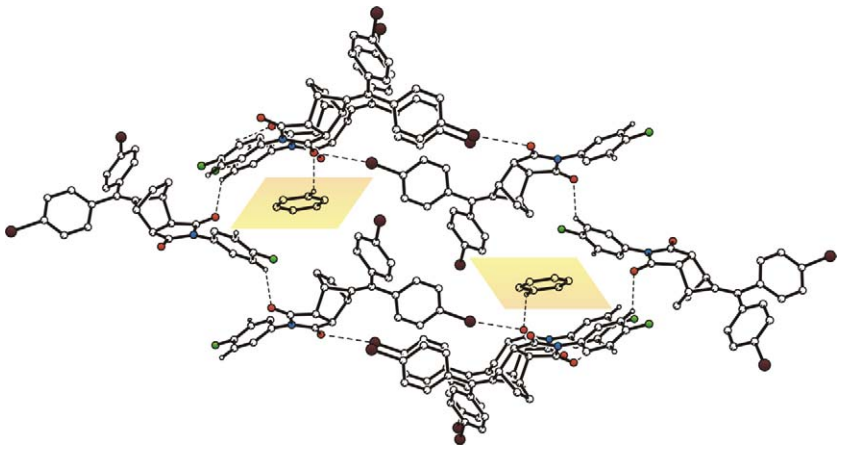


Fig. 6. Packing diagram of compound **14**·C_6H_6 along the *a*-axis. Non-covalent interactions are represented as broken lines.

of intermolecular O···Br contacts [31]. They give rise to the generation of a ring system consisting of six molecules of **14**. This particular kind of halogen bonding where halogens (electron acceptor site) contact to atoms containing lone pairs (electron donor site) is currently a topic of great promise in crystal engineering [32,33]. The parameters of the present Br···O contact (3.23 Å, 169.1° and 119.5°) coincide with the modern theoretical interpretation of this particular interaction (effect of the σ-hole) [34]. Besides this specific Br···O interactions, different C–H···O (F) contacts determine the crystalline packing of **14**·C_6H_6 (Fig. 6).

Except the special bromo involved interaction, corresponding C–H···O(F) contacts are also typical of the packing structures of the non-solvated compounds **13**, **17** and **18**. Remarkably, it is the fluorine-free derivative **13** which exhibits the shortest distance of the C–H···O contacts (C14–H14···O2, 2.31 Å, 165.7°), generating a dimer that bridges zigzag chains caused by a weaker C–H···O contact (C8–H8···O1, 2.62 Å, 107.2°). From size consideration, substitution of a hydrogen for a fluorine atom does not considerably enlarge the molecular volume. On the other hand, the charge distribution in the molecule will change significantly by this kind of modification and hence also the attractive and repulsive forces between adjacent molecules. As a result of the repulsive forces between fluorine atoms, creating dimers of molecules is hampered in the case of a high fluorine substitution. Moreover, with an increasing number of fluorine atoms, being added to the large bromine substituents in the molecular structure, it is an obvious conclusion that C–H···π contacts [4] are increasingly restraint. This behaviour is clearly manifested with the structures of the compounds **13**, **14**·C_6H_6, **17** and **18**, respectively. The minor role of C–H···π-contacts in the crystal structures of these compounds is also shown with the rather long distances involving the hydrogen atom and the centre of the aromatic ring. While the mean distance is found as 2.93 Å in the present compounds, the corresponding values for **1**–**6** (2.88 Å) and **7**–**12** (2.79 Å) are shorter. Furthermore, the present compounds are mainly incorporated into zigzag chains and chains, mostly extended along the crystallographic *b*-axis and always being in combination with C–H···O(F)-contacts. Nevertheless, whether or not these contacts are more a consequence of the other supramolecular interactions or a result of close packing effects in the crystal lattice remains a matter for discussion.

2.3. Isostructurality calculations

The cell similarity (π), the isostructurality [*Is*] as well as the molecular isometricity indices [*Im*] were calculated for those compounds making possible a reasonable numerical comparison [35–38]. Within this frame, the effects of the different degree of fluorination on the *N*-phenyl ring and the halogenation of the methylidene bound phenyl groups on the packing arrangements of the molecules were investigated. All compounds crystallize in the monoclinic crystal system with both centrosymmetric ($P2_1/c$, $P2_1/n$, $C2/c$) and chiral space groups ($P2_1$, $C2$). Systematics regarding the effect of halogenation on the molecular conformation and as a result from the packing arrangement are revealed.

The presence of H, F or Br in *para*-position of the methylidene bound phenyl rings markedly influences the space group of the crystal (Table S1, SI). The plain molecules **1**–**6** crystallize in the $P2_1$ space group, with two exceptions (**1** and **4**) where space group $P2_1/c$ appears. On the other hand, the F substituted molecules **7**–**12** prefer the $P2_1/c$ (or $P2_1/n$) arrangement, excepting **9** which shows the space group $P2_1$. The Br substitution seems to have the greatest effect on the packing. Although the *N*-phenyl non-fluorinated compound **13** shows the space group $P2_1/c$, those being fluorinated crystallize in space groups $C2/c$ (**17**), $C2$ (**18**), and enclathrate the solvent molecule (**14**·C_6H_6) or resist suitable crystal formation (**15**, **16**). Moreover, influences of the placement and degree of fluorine substitution of the *N*-phenyl subunit on the space group of the crystal are observed. The $P2_1$ structures (Fig. 7) show two different kinds of assemblies: (1) the *para* **2** and *ortho–para* **5**, and (2) the *meta* (**3**, **9**) fluoro substituted crystals, which are the most similar. The $P2_1/c$ ($P2_1/n$) structures (Fig. S2, SI) can be divided into three subgroups: (1) the non-substituted **1** and *ortho* **4**, **10**, (2) the non-substituted **7**, **13**, the *para* **8**, and the *ortho–para* substituted **11**, as well as (3) the *ortho–meta–para* derivative **12**. However, the most different compounds are the perfluorinated ones. The compound **6** contains two molecules in the asymmetric unit, **12** is distinctly different but keeps the $P2_1/n$ space group while **18** appears in the $C2$ space group.

The fluorination of the *N*-phenyl ring, the molecular conformation (Table 1) and the packing arrangements can be well correlated. Four different types of molecular conformations can be distinguished characterized by the interplanar angles of the phenyl rings (Table 2). The *para* and *ortho–para* *N*-phenyl F substituted molecules with plain methylidene bound phenyl groups shows the type I molecular conformation in space group $P2_1$. The *meta* *N*-phenyl F substitution results in the type II molecular conformation in space group $P2_1$. A fluorine-free *N*-phenyl subunit, independent of the particular methylidene bound phenyl groups, leads to either type III or IV conformation in space group $P2_1/c$. The *ortho* *N*-phenyl F substituted molecules reveal type III conformation, while the *ortho* and *ortho–para* *N*-phenyl F substitutions result in the type IV conformation. The perfluorinated molecules **6** and **12** differ the most from the other members of the series. There are two

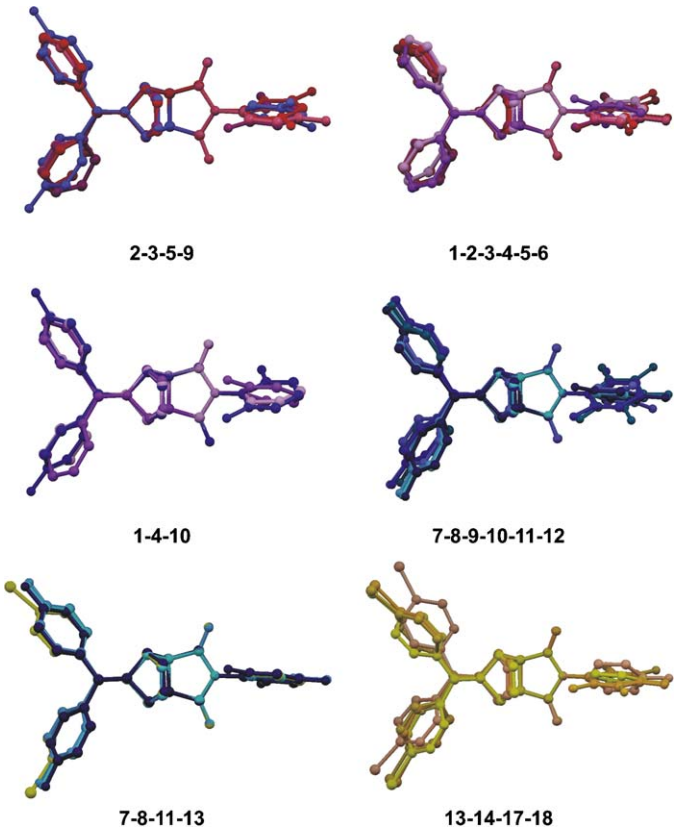


Fig. 7. Superimposed molecules (**1**–**14**, **17**, **18**) from different structures. Only rings M are fitted in the figures to enhance the visualization of the conformational differences.

crystallographically independent molecules in the asymmetric unit of **6** ($Z' = 2$), one of them is close to the type III, the other one is close to the type IV conformation. The unit cell of **12** is significantly larger than for the other members in the series of the *para* F substituted methylidene bound phenyl group containing compounds **7**–**11** with a molecular conformation close to the type III. Bromine substitution of the methylidene bound phenyl groups has a substantial increased space requirement which gives more freedom to the set of molecular conformations. Compound **13** belongs to the type IV conformation, although it is the most deviating of this type class. The compound **14** enclathrates a benzene solvent molecule, while it was not possible to grow single crystals from **15** and **16**, and **17** and **18** crystallize in the space groups *C*2/*c* and *C*2, respectively. Thus these latter compounds can hardly be categorized to the previous types of molecular conformation.

Table 2
Types of molecular conformation observed in the investigated series of compounds. Typical values of the interplanar angles in the different conformational types are given[a].

Conformation type	I	II	III	IV
Structures	**2**, **5**	**3**, **9**	**1**, **4**, **10**	**7**, **8**, **11**, **13**
B–C (°)	81	85	87	82
M–B (°)	50	44	70	54
M–C (°)	53	71	44	60
	M–B < M–C	M–B ≪ M–C	M–B ≫ M–C	M–B < M–C
|M–B – M–C| (°)	~3	~27	~26	~9
Space group	$P2_1$	$P2_1$	$P2_1/c$	$P2_1/c$
N-Phe substitution	p, o-p	m, m	-, o, o	-, p, o-p, -

[a] The ring mean planes are labelled as M: N1/C7–C10; B: C17–C22; C: C23–C28 (Scheme 1).

Table 3
Cell similarity (π), isostructurality [$I(s)$] and molecular isometricity indices [$I(m)$] calculated within the group of conformational categories for 31 and 12 atoms, respectively.

Space group	Structure	π	*Is* (31) %	*Is* (12) %	*Im* (31) %
$P2_1$	**2**/**5**	0.01434	78.9	84.1	99.05
	3/**9**	0.00744	–	55.4	84.14
$P2_1/c$	**1**/**4**	0.00066	66.9	73.2	94.43
	1/**10**	0.02518	54.3	67.7	90.73
	4/**10**	0.02582	78.0	87.4	99.12
	7/**8**	0.01432	90.8	93.4	99.43
	7/**11**	0.00510	79.2	76.0	98.98
	7/**13**	0.02408	27.0	25.4	99.07
	8/**11**	0.00936	76.2	73.0	97.83
	8/**13**	0.00990	27.6	27.5	98.55
	11/**13**	0.01908	22.4	25.3	99.35

Cell similarity, isostructurality and molecular isometricity calculations were carried out considering the conformational categories (Table 3). Isostructurality calculations were performed on two different levels. In one case, 31 heavy atoms including all C, N and O atoms but excluding any halogen, were taken into account. In the other case, a restriction was imposed using only the 12 core atoms (N1, O1, O2, C7, C8, C9, C10, C11, C12, C13, C14, C15) since the calculation with this rigid framework gives more information on the positional differences and eliminates the effect of the rotation of the phenyl rings. Molecular similarity is calculated with the least squares fit of the 31 non-halogen heavy atoms. Within a respective conformational category, the R^4 substituents on the methylidene bound phenyl rings exercise the most significant effect: as the size of R^4 increases, the similarity of $I(s)$ and $I(m)$ considerably decreases (Fig. 7).

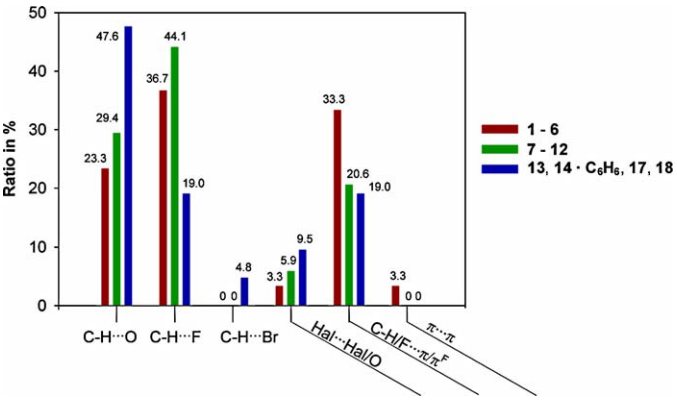
3. Comparative reflection and conclusions

The present series of systematically fluorine substituted molecules show specific changes in the packing arrangements to a substantial extent. The compounds with two plain phenyl rings attached to the methylidene group crystallize mainly in the space group $P2_1$, while the respective *para*-fluorinated phenyl derivatives prefer the space group $P2_1/c$. Considering the series of bromine substituted compounds, the most different space groups are observed, if compounds yield suitable crystals at all.

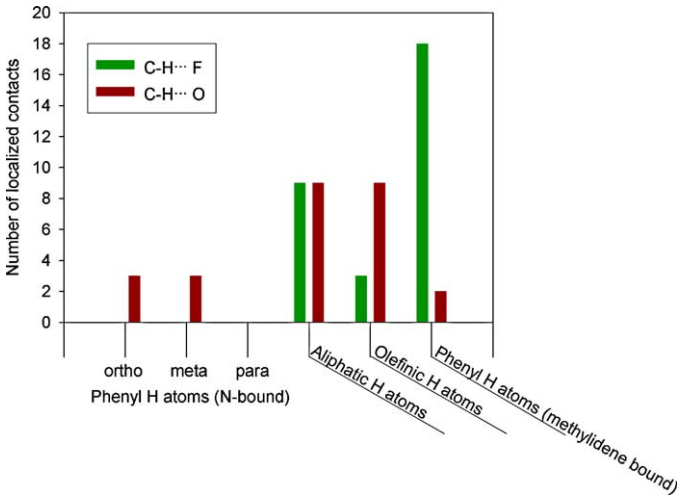
The placement of the molecule in the unit cell is mainly determined by the molecular conformation which is essentially governed by the mode of fluorine substitution of the *N*-phenyl ring. The packing arrangements can be classified into four categories. They are similar in the cases of the *ortho* and the *ortho–para* fluorine substituted molecules, and also in case of the *meta* substitution, while the *ortho–meta–para* perfluorinated compounds are the most different ones. Although the effects of halogenation of the molecules on the crystal structures are not strictly systematic, tendencies are revealed that may be useful in crystal structure prediction.

Rating the influence of the fluorine and bromine substitution in regard of their competition with stronger hydrogen acceptors, such as oxygen, nitrogen and the π system, provides the following facts. Contrary to the prevailing opinion that the aryl-perfluoroaryl intermolecular stacking arrangement behaves as a rather robust synthon [5,14], an interaction of this type has not been determined as a relevant binding motif in the present crystal structures. This particular finding corresponds with a previous observation [21]. However, there is a distinct balance of hydrogen interactions to oxygen and fluorine atoms and significant C–H···π contacts.

A more detailed comparison in this respect yields the following data. As shown in Scheme 3, the ratio of C–H···O interactions



Scheme 3. Ratio of intermolecular contacts based on the crystal structures; allocated to the compound classes.



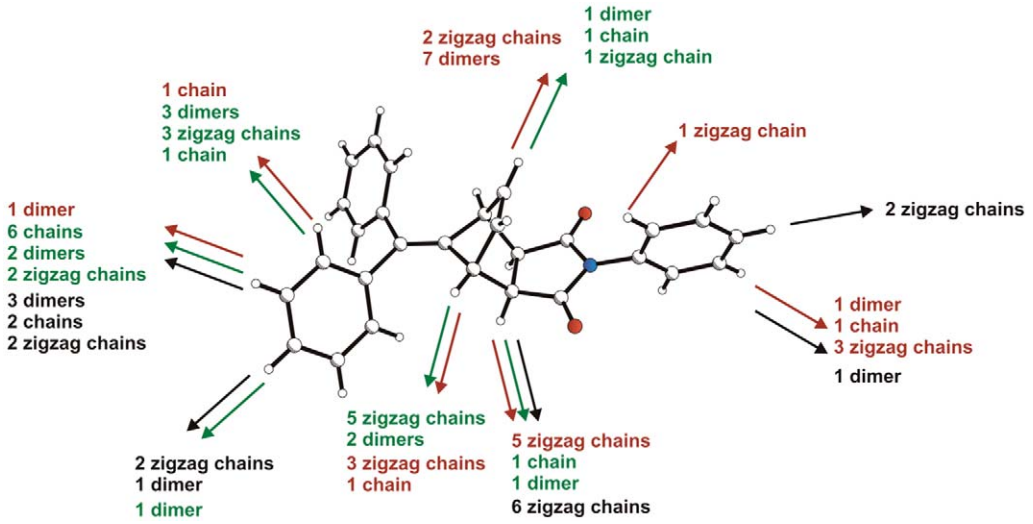
Scheme 4. Diagram showing the relevant intermolecular C–H···F (green) and C–H···O (red) contacts of the different compounds dependent on the hydrogen atom position. (For interpretation of the references to color in this scheme, the reader is referred to the web version of the article.)

increases only slightly with the introduction of fluorine in the methylidene bound phenyl rings (**7**–**12**) but reaches almost half of the number of all localized contacts with the corresponding bromine substitution (**13**, **14**·C_6H_6, **17**, **18**). This increase of the number of C–H···O interactions goes with the decrease in the number of C–H/X···π/π^F contacts. However, unlike the C–H···O interactions, the C–H···π contacts are rather constant in their length and hence potentially also in their strength. As a result of the fluorine substitution of the methylidene bound phenyl rings, the number of C–H···F interactions increases up to 44% but drops down rapidly to 19% with the alternative bromine substitution. The F···F contacts observed in the crystal structures are rather secondary and mostly determined by the packing, while C–F···π^F ^{F} are not present at all.

Additional information arises from a more specific comparison of the C–H···O and C–H···F contacts. These were previously found to depend significantly on the position of the hydrogen atom in the respective molecules of fluorinated maleimides and phthalimides [21]. As a result, it was shown that the fluorine atom is more specific than oxygen in making its choice to contact a hydrogen atom. In particular, it appeared that hydrogen atoms bonded to the already fluorinated aromatic ring are at a disadvantage with reference to other hydrogen atoms, such as olefinic ones, in the formation of C–H···F contacts. This behaviour is also becoming visible in the present study. Actually, as can be taken from Scheme 4, there is no C–H···F interaction with a hydrogen atom of a fluorinated phenyl ring but only with aliphatic or olefinic hydrogens and especially with hydrogen atoms of the methylidene bound phenyl rings. The oxygen atoms show a less specific behaviour but prefer aliphatic and olefinic H atoms.

Another point of interest relates to the particular modes of interaction represented in Scheme 5. Hydrogen atoms of the *N*-substituted phenyl ring prefer contacts in the kind of zigzag chains to oxygen atoms or the π system. The same behaviour is found for the C–H···O– and C–H···F interactions involving the aliphatic H atoms, while the corresponding contacts with olefinic and aromatic hydrogen atoms do not demonstrate such a clear specification of the interaction modes.

In summary, we conclude that even in the case of a systematic substitution of hydrogen for fluorine atoms in a favourable model compound, such as shown with the series of highly rigid Diels–Alder adducts **1**–**18**, it is presently not possible to accurately correlate the crystallization outcome with the particular pattern of



Scheme 5. Diagram showing the motifs of intermolecular C–H···F (green), C–H···O (red) and C–H···π (black) contacts dependent on the hydrogen atom position, demonstrated with the parent model molecules irrespective of the fluorine substitution. Motifs are chains, zigzag chains and dimers. The digits depict the number of motifs found in compounds **1**–**13**, **14**·C_6H_6, **17** and **18**. (For interpretation of the references to color in this scheme, the reader is referred to the web version of the article.)

fluorine substitution and the influence of a few selected other heteroatoms. Owing to the rather weak interactions emanating from the fluorine contacts, different modes of fluorine interactions compete between each other and are also in a competition with the interaction sites of the other potential acceptor groups. Thus the finding of a predetermined pattern of fluorine involved supramolecular interactions remains still a difficult problem. Nevertheless, the crystalline packing structures of the organic fluorine compounds, studied here, indicate some trends in the observed interaction modes as specified above. In particular it should be pointed out that although potential opportunities to form $\pi^H\cdots\pi^F$ interactions between some of the molecules (e.g. **5**, **6**) are given, they are not realized in the corresponding structures. This is in contradiction to the generally held view on the $\pi^H\cdots\pi^F$ stacking interaction, being understood as a so-called robust supramolecular synthon [5,14]. Obviously, this kind of interaction requires in addition to the mere presence of π^H and π^F involved subunits a more planar overall structure of the molecule to become effective, which is not fulfilled here. A further remarkable fact is that the bromine atoms, although being easy to access due to their peripheral location, are no effective competitors with the other heteroatoms giving rise to Br···X (N, O [33,34] or Br···Br contacts [20c]).

4. Experimental

4.1. General

Melting points were determined using a microscope heating stage PHMK Rapido (VEB Wägetechnik). IR spectra were measured on FT-IR 510 Nicolet as KBr pellets. ^{1}H, ^{13}C and ^{19}F NMR spectra were measured in chloroform solution at room temperature on a Bruker Avance DPX 400 at 400, 100 and 376 MHz, respectively. Elemental analyses were performed on a Heraeus CHN rapid analyzer. Mass spectra were recorded with ESQUIRE-LC ion trap, solvent: acetonitrile/water/0.1% formic acid; flow rate 3 μL/min; ion polarity: positive.

All *N*-phenylmaleimides **19a**–**f** (Scheme 2) were prepared from the corresponding aniline and maleic anhydride according to the literature [20]. The diarylfulvenes **20a**–**c** (Scheme 2) were obtained following reported procedures [24].

4.2. Syntheses of compounds 1–18

To a stirred solution of the respective *N*-phenylmaleimide (10 mmol) in benzene (25 mL), a solution of the corresponding diarylfulvene (10 mmol) in benzene (25 mL) was added. The mixture was heated to reflux for 5 h and allowed to cool down to room temperature. The solid precipitate which has formed was collected and dried in vacuum. Recrystallization of the crude product from acetone yielded the pure compounds as colourless solids. Specific details for each compound are given below.

4.2.1. *N*-Phenyl-7-(diphenylmethylidene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (1)

N-Phenylmaleimide (**19a**) (1.73 g, 10 mmol) and diphenylfulvene (**20a**) (2.30 g, 10 mmol) were used. Yield 1.30 g (32%); mp: 236 °C (dec.), lit. [22] mp: 123 °C. Anal. Calcd. for $C_{28}H_{21}NO_2$: C, 83.35; H, 5.25; N, 3.47; Found: C, 83.43; H, 5.28; N, 3.29%. IR (KBr): ν_{max} (cm^{-1}) 3074 (CH_{Ar}), 3022 ($CH_{C=C}$), 1776, 1704 (C=O), 1621 (C=C), 1598, 1497 ($C=C_{Ar}$). ^{1}H NMR ($CDCl_3$): δ_H 7.44–7.09 (m, 15H, Ar–H), 6.50 (s, 2H, HC=CH), 4.03 (s, 2H, H-6), 3.61 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$) δ_C 175.73 (C=O), 151.4 (C-7), 140.0 (C-9), 135.2 (HC=CH), 131.8 (C-4), 129.4 (C-10), 129.1 (C-3), 128.7 (C-1), 128.2 (C-11), 127.3 (C-12), 126.6 (C-2), 123.9 (C-8), 46.8 (C-6), 44.9 (C-5). MS (ESI) *m*/*z*: 404 $[M+H]^+$ 100%.

4.2.2. *N*-(4-Fluorophenyl)-7(diphenylmethylidene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (2)

N-(4-Fluorophenyl)maleimide (**19b**) (1.91 g, 10 mmol) and diphenylfulvene (**20a**) (2.30 g, 10 mmol) were used. Yield 1.49 g (35%); mp: 215 °C (dec.). Anal. Calcd. for $C_{28}H_{20}FNO_2$: C, 79.79; H, 4.78; N, 3.32; Found: C, 79.95; H, 4.80; N, 3.11%. IR (KBr): ν_{max} (cm^{-1}) 3089 (CH_{Ar}), 3022 ($CH_{C=C}$), 1773, 1708 (C=O), 1627 (C=C), 1601, 1512 ($C=C_{Ar}$), 1387, 1181 (C–N–C). ^{1}H NMR ($CDCl_3$): δ_H 7.35–7.08 (m, 14H, Ar–H), 6.48 (s, 2H, HC=CH), 4.02 (s, 2H, H-6), 3.59 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 175.6 (C=O); 162.2 (d, C-1, $^1J_{CF}$ = −249.5 Hz), 151.3 (C-7), 140.0 (C-9), 135.1 (HC=CH), 129.4 (C-10), 128.37 (C-3), 128.2 (C-11), 127.3 (C-12), 127.7 (C-4), 124.0 (C-8), 116.1 (d, C2, $^2J_{CF}$ = 23.0 Hz), 46.7 (C-6), 44.8 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −112.8 (m, F-1). MS (ESI) *m*/*z*: 422 $[M+H]^+$ 100%.

4.2.3. *N*-(3,5-Difluorophenyl)-7-(diphenylmethylidene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (3)

N-(3,5-Difluorophenyl)maleimide (**19c**) (2.09 g, 10 mmol) and diphenylfulvene (**20a**) (2.30 g, 10 mmol) were used. Yield: 1.74 g (40%); mp: 225–226 °C (dec.). Anal. Calcd. for $C_{28}H_{19}F_2NO_2$: C, 76.53; H, 4.36; N, 3.19; Found: C, 76.57; H, 4.40; N, 3.01%. IR (KBr): ν_{max} (cm^{-1}) 3084 (CH_{Ar}), 3022 ($CH_{C=C}$), 1775, 1712 (C=O), 1620 (C=C), 1607, 1475 ($C=C_{Ar}$). ^{1}H NMR ($CDCl_3$): δ_H 7.35–6.81 (m, 13H, Ar–H), 6.48 (s, 2H, HC=CH), 4.02 (s, 2H, H-6), 3.60 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 174.9 (C=O), 162.8 (d, C-2, $^1J_{CF}$ = −249.5 Hz), 151.0 (C-7), 139.9 (C-9), 135.2 (HC=CH), 133.7 (C-4), 129.3 (C-10), 128.3 (C-11), 127.4 (C-12), 124.2 (C-8), 110.1 (d, C-3, $^2J_{CF}$ = 27.9 Hz), 104.2 (t, C-1, $^2J_{CF}$ = 25.2 Hz), 46.9 (C-6), 44.9 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −108.9 (m, F-2). MS (ESI) *m*/*z*: 440 $[M+H]^+$ 100%.

4.2.4. *N*-(2,6-Difluorophenyl)-7-(diphenylmethylidene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (4)

N-(2,6-Difluorophenyl)maleimide (**19d**) (2.09 g, 10 mmol) and diphenylfulvene (**20a**) (2.30 g, 10 mmol) were used. Yield: 1.64 g (37%); mp: 234–236 °C (dec.). Anal. Calcd. for $C_{28}H_{19}F_2NO_2$: C, 76.53; H, 4.36; N, 3.19; Found: C, 76.67; H, 4.37; N, 3.03%. IR (KBr): ν_{max} (cm^{-1}) 3080 (CH_{Ar}), 3023 ($CH_{C=C}$), 1782, 1717 (C=O), 1622 (C=C), 1598, 1477 ($C=C_{Ar}$). ^{1}H NMR ($CDCl_3$): δ_H 7.39–6.81 (m, 13H, Ar–H), 6.52 (s, 2H, HC=CH), 4.00 (s, 2H, H-6), 3.67 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 174.1 (C=O), 158.33 (d, C-3, $^1J_{CF}$ = −256.5 Hz), 151.2 (C-7), 140.0 (C-9), 135.2 (HC=CH), 131.0 (C-1), 129.4 (C–10), 128.2 (C-11), 127.3 (C-12), 124.1 (C-8), 112.1 (d, C-2, $^2J_{CF}$ = 19.6 Hz), 109.2 (C-4), 46.7 (C-6), 45.7 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −115.4 (m, F-3-syn), −117.55 (m, F-3-anti). MS (ESI) *m*/*z*: 440 $[M+H]^+$ 100%.

4.2.5. *N*-(2,4,6-Trifluorophenyl)-7-(diphenylmethylidene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (5)

N-(2,4,6-Trifluorophenyl)maleimide (**19e**) (2.27 g, 10 mmol) and diphenylfulvene (**20a**) (2.30 g, 10 mmol) were used. Yield: 2.19 g (48%); mp: 246–247 °C (dec.). Anal. Calcd. for $C_{28}H_{18}F_3NO_2$: C, 73.52; H, 3.97; N, 3.06; Found: C, 73.69; H, 4.01; N, 2.90%. IR (KBr): ν_{max} (cm^{-1}) 3079 (CH_{Ar}), 3022 ($CH_{C=C}$), 1790, 1724 (C=O), 1632 (C=C), 1608, 1518 ($C=C_{Ar}$). ^{1}H NMR ($CDCl_3$): δ_H 7.41–7.32 (m, 6H, H-11, H-12), 7.17–7.15 (m, 4H, H10), 6.85 (m, 2H, H-2), 6.55 (s, 2H, HC=CH), 4.07 (s, 2H, H-6), 3.74 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 174.0 (C=O), 164.3, 161.7 (d, C-1, $^1J_{CF}$ = −253.0 Hz), 158.7 (d, C-3, $^1J_{CF}$ = −255.7 Hz), 151.1 (C-7), 140.0 (C-9), 135.3 (HC=CH), 129.4 (C-10), 128.3 (C-11), 127.4 (C-12), 124.3 (C-8), 105.9 (C-4), 101.1 (t, C-2, $^2J_{CF}$ = 25.2 Hz), 46.7 (C-6), 45.7 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −104.9 (m, F-1), −112.1 (m, F-3-syn), −114.9 (m, F-3-anti). MS (ESI) *m*/*z*: 458 $[M+H]^+$ 100%.

4.2.6. N-(2,3,4,5,6-Pentafluorophenyl)-7-(diphenylmethylidene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (6)

N-2,3,4,5,6-(Pentafluorophenyl)maleimide (**20f**) (2.63 g, 10 mmol) and diphenylfulvene (**20a**) (2.30 g, 10 mmol) were used. Yield: 1.79 g (36%); mp: 211–216 °C (dec.). Anal. Calcd. for $C_{28}H_{16}F_5NO_2$: C, 68.16; H 3.27; N, 2.84; Found: C, 68.16; H, 3.28; N, 2.70%. IR (KBr): ν_{max} (cm^{-1}) 3081 (CH_{Ar}), 3024 ($CH_{C=C}$), 1789, 1729 (C=O), 1627 (C=C), 1522, 1492 ($C=C_{Ar}$). ^1H NMR ($CDCl_3$): δ_H 7.35–7.27 (m, 6H, H-11, H-12), 7.10–7.08 (m, 4H, H10), 6.49 (s, 2H, HC=CH), 4.02 (s, 2H, H-6), 3.72 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 173.3 (C=O), 150.7 (C-7), 143.5 (d, C-3, $^1J_{CF}$ = −255.5 Hz), 142.2 (d, C-1, $^1J_{CF}$ = −257.5 Hz), 139.9 (C-9), 137.9 (d, C-2, $^1J_{CF}$ = −255.5 Hz), 135.3 (HC=CH), 129.3 (C-10), 128.3 (C-11), 127.5 (C-12), 124.6 (C-8), 107.0 (C-4), 46.8 (C-6), 45.9 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −141.5 (m, F-3-syn), −143.5 (m, F-3-anti), −151.7 (m, F-1), −161.5 (m, F-2). MS (ESI) *m*/*z*: 494 $[M+H]^+$ 100%.

4.2.7. N-Phenyl-7-[bis(4-fluorophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (7)

N-Phenylmaleimide (**19a**) (1.73 g, 10 mmol) and bis(4-fluorophenyl)fulvene (**20b**) (2.66 g, 10 mmol) were used. Yield: 1.40 g (32%); mp: 239 °C (dec.). Anal. Calcd. for $C_{28}H_{19}F_2NO_2$: C, 76.53; H, 4.36; N, 3.19; Found: C, 76.64; H, 4.32; N, 2.97%. IR (KBr): ν_{max} (cm^{-1}) 3058 (CH_{Ar}), 1771, 1708 (C=O), 1599, 1507 ($C=C_{Ar}$), 1382, 1187 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.45–7.02 (m, 13H, Ar–H), 6.50 (s, 2H, HC=CH), 3.97 (s, 2H, H-6), 3.58 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 175.5 (C=O), 162.1 (d, C-12, $^1J_{CF}$ = −247.5 Hz), 151.6 (C-7), 135.8 (C-9), 135.1 (HC=CH), 131.7 (C-4), 130.9 (C-10), 129.2 (C-3), 128.8 (C-1), 126.5 (C-2), 121.9 (C-8), 115.4 (d, C-11, $^2J_{CF}$ = 21.5 Hz), 46.7 (C-6), 44.8 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −115.0 (m, F-12). MS (ESI) *m*/*z*: 440 $[M+H]^+$ 100%.

4.2.8. N-(4-Fluorophenyl)-7-[bis(4-fluorophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (8)

N-(4-Fluorophenyl)maleimide (**19b**) (1.91 g, 10 mmol) and bis(4-fluorophenyl)fulvene (**20b**) (2.66 g, 10 mmol) were used. Yield: 2.38 g (52%); mp: 211 °C (dec.). Anal. Calcd. for $C_{28}H_{18}F_3NO_2$: C, 73.52; H, 3.97; N, 3.06; Found: C, 73.40; H, 3.98; N, 2.92%. IR (KBr): ν_{max} (cm^{-1}) 3068 (CH_{Ar}), 3012 ($CH_{C=C}$), 1775, 1714 (C=O), 1601, 1508 ($C=C_{Ar}$), 1383, 1184 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.27–7.00 (m, 8H, Ar–H), 6.49 (s, 2H, HC=CH), 3.98 (s, 2H, H-6), 3.58 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 175.4 (C=O), 162.2 (d, C-1, $^1J_{CF}$ = −248.5 Hz), 162.1 (d, C-12, $^1J_{CF}$ = −247.5 Hz), 151.5 (C-7), 135.7 (C-9), 135.09 (HC=CH), 130.9 (C-10), 128.3 (C-3), 127.6 (C-4), 122.0 (C-8), 116.1 (d, C-2, $^2J_{CF}$ = 22.9 Hz), 115.3 (d, C-11, $^2J_{CF}$ = 21.5 Hz), 46.7 (C-6), 44.7 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −112.7 (m, F-1), −114.9 (m, F-12). MS (ESI) *m*/*z*: 458 $[M+H]^+$ 100%.

4.2.9. N-(3,5-Difluorophenyl)-7-[bis(4-fluorophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (9)

N-(3,5-Difluorophenyl)maleimide (**19c**) (2.09 g, 10 mmol) and bis(4-fluorophenyl)fulvene (**20b**) (2.66 g, 10 mmol) were used. Yield: 2.20 g (46%); mp: 224 °C (dec.). Anal. Calcd. for $C_{28}H_{17}F_4NO_2$: C, 70.74; H, 3.60; N, 2.95; Found: C, 70.81; H, 3.76; N, 2.89%. IR (KBr): ν_{max} (cm^{-1}) 3094 (CH_{Ar}), 1776, 1712 (C=O), 1621 (C=C), 1604, 1507 ($C=C_{Ar}$), 1397, 1181 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 8.12 (2H, H-3, s), 7.05–7.03 (m, 7H, Ar–H), 6.49 (s, 2H, HC=CH), 3.99 (s, 2H, H-6), 3.59 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 174.7 (C=O), 162.8 (d, C-2, $^1J_{CF}$ = −249.5 Hz), 162.2 (d, C-12, $^1J_{CF}$ = −247.5 Hz), 151.3 (C-7), 135.7 (C-9), 135.2 (HC=CH), 133.6 (C-4), 130.9 (C-10), 122.2 (C-8), 115.4 (d, C–11, $^2J_{CF}$ = 21.5 Hz), 110.0 (d, C-3, $^2J_{CF}$ = 27.8 Hz), 104.3 (t, C-1, $^2J_{CF}$ = 25.2 Hz), 46.8 (C-6), 44.8 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −108.8 (m, F-2), −114.8 (m, F-12). MS (ESI) *m*/*z*: 476 $[M+H]^+$ 100%.

4.2.10. N-(2,6-Difluorophenyl)-7-[bis(4-fluorophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (10)

N-(2,6-Difluorophenyl)maleimide (**19d**) (2.09 g, 10 mmol) and bis(4-fluorophenyl)fulvene (**20b**) (2.66 g, 10 mmol) were used. Yield: 2.85 g (60%); mp: 237 °C (dec.). Anal. Calcd. for $C_{28}H_{17}F_4NO_2$: C, 70.74; H, 3.60; N, 2.95; Found: C, 70.88; H, 3.59; N, 3.01%. IR (KBr): ν_{max} (cm^{-1}) 3063 (CH_{Ar}), 3017 ($CH_{C=C}$), 1781, 1721 (C=O), 1600, 1505 ($C=C_{Ar}$), 1374, 1198 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.43–7.00 (m, 11H, Ar–H), 6.52 (s, 2H, HC=CH), 3.99 (s, 2H, H-6), 3.69 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 173.9 (C=O), 162.1 (d, C-12, $^1J_{CF}$ = −247.5 Hz), 158.5 (d, C-3, d, $^1J_{CF}$ = −241.4 Hz), 151.5 (C-7), 135.8 (C-9), 135.2 (HC=CH); 131.2 (C-1), 130.9 (C-10), 122.2 (C-8), 115.3 (d, C-11, $^2J_{CF}$ = 21.5 Hz), 112.1 (d, C-2, $^2J_{CF}$ = 19.9 Hz), 109.2 (C-4), 46.6 (C-6), 45.6 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −114.9 (m, F-12), −115.5 (m, F-3-syn), −117.7 (m, F-3-anti). MS (ESI) *m*/*z*: 476 $[M+H]^+$ 100%.

4.2.11. N-(2,4,6-Trifluorophenyl)-7-[bis(4-fluorophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (11)

N-(2,4,6-Trifluorophenyl)maleimide (**19e**) (2.27 g, 10 mmol) and bis(4-fluorophenyl)fulvene (**20b**) (2.66 g, 10 mmol) were used. Yield: 1.91 g (39%); mp: 205–207 °C (dec.). Anal. Calcd. for $C_{28}H_{16}F_5NO_2$: C, 68.16; H, 3.27; N, 2.84; Found: C, 68.24; H, 3.27; N, 2.93%. IR (KBr): ν_{max} (cm^{-1}) 3048 (CH_{Ar}), 1782, 1724 (C=O), 1610, 1507 ($C=C_{Ar}$), 1393, 1184 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.08–7.00 (m, 8H, H10, H-11), 6.79 (m, 2H, H-2), 6.48 (s, 2H, HC=CH), 3.97 (s, 2H, H-6), 3.66 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 173.8 (C=O), 163.0 (d, C-1, $^1J_{CF}$ = −252.5 Hz), 162.1 (d, C-12, $^1J_{CF}$ = −248.5 Hz), 158.7 (d, C-3, $^1J_{CF}$ = −255.5 Hz), 151.3 (C-7), 135.8 (C-9), 135.2 (HC=CH), 130.9 (C-10), 122.2 (C-8), 115.3 (d, C-11, $^2J_{CF}$ = 21.5 Hz), 105.8 (t, C-4, $^2J_{CF}$ = 17.6 Hz), 101.1 (t, C-2, $^2J_{CF}$ = 25.7 Hz), 46.6 (C-6), 45.6 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −104.7 (m, F-1), −112.2 (m, F-3-syn), −114.2 (m, F-3-anti), −114.9 (m, F-12). MS (ESI) *m*/*z*: 494 $[M+H]^+$ 100%.

4.2.12. N-(2,3,4,5,6-Pentafluorophenyl)-7-[bis(4-fluorophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (12)

N-(2,3,4,5,6-Pentafluorophenyl)maleimide (**19f**) (2.63 g, 10 mmol) and bis(4-fluorophenyl)fulvene (**20b**) (2.66, 10 mmol) were used. Yield: 4.39 g (83%); mp: 188 °C (dec.). Anal. Calcd. for $C_{28}H_{14}F_7NO_2$: C, 63.52; H, 2.67; N, 2.65; Found: C, 63.61; H, 2.64; N, 2.71%. IR (KBr): ν_{max} (cm^{-1}) 3053 (CH_{Ar}), 3012 ($CH_{C=C}$), 1781, 1731 (C=O), 1601, 1523 ($C=C_{Ar}$), 1361, 1178 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.12–7.03 (m, 8H, Ar–H), 6.50 (s, 2H, HC=CH), 3.98 (s, 2H, H-6), 3.70 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 173.1 (C=O), 162.2 (d, C-12, $^1J_{CF}$ = −247.7 Hz), 151.0 (C-7), 143.5 (d, C-3, $^1J_{CF}$ = −254.5 Hz), 142.2 (d, C-1, $^1J_{CF}$ = −257.5 Hz), 137.9 (d, C-2, $^1J_{CF}$ = −253.5 Hz), 135.6 (C-9), 135.3 (HC=CH), 130.9 (C-10), 122.6 (C-8), 115.4 (d, C-11, $^2J_{CF}$ = 21.5 Hz), 107.0 (C-4), 46.7 (C-6), 45.8 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −114.7 (m, F-12), −141.6 (m, F-3-syn), −143.5 (m, F-3-anti), −151.5 (m, F-1), −161.4 (m, F-2). MS (ESI) *m*/*z*: 530 $[M+H]^+$ 100%.

4.2.13. N-Phenyl-7-[bis(4-bromophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (13)

N-Phenylmaleimide (**19a**) (1.73 g, 10 mmol) and bis (4-bromophenyl)fulvene (**20c**) (3.90 g, 10 mmol) were used. Yield:

2.25 g (40%); mp: 229 °C (dec.). Anal. Calcd. for $C_{28}H_{19}Br_2NO_2$: C, 59.92; H, 3.41; N, 2.50; Found: C, 59.97; H, 3.40; N, 2.36%. IR (KBr): ν_{max} (cm^{-1}) 3068 (CH_{Ar}), 3017 ($CH_{C=C}$), 1775, 1713 (C=O), 1595, 1488 (C=C_{Ar}), 1387, 1184 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.51–6.93 (m, 13H, Ar–H), 6.48 (s, 2H, HC=CH), 3.96 (s, 2H, H-6), 3.55 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$) δ_C 175.3 (C=O), 152.3 (C-7), 138.3 (C-9), 135.0 (HC=CH), 131.6 (C-10), 131.0 (C-11), 129.1 (C-3), 128.8 (C-1), 128.3 (C-4), 126.50 (C-2), 121.8, 121.7 (C-8, C12), 46.7 (C-6), 44.6 (C-5). MS (ESI) *m/z*: 562 $[M+H]^+$ 100%.

4.2.14. *N-(4-Fluorophenyl)-7-[bis(4-bromophenyl)methylidene]bicycle[2.2.1]hept-2-ene-5,6-dicarboximide (**14**)*

N-(4-Fluorophenyl)maleimide (**19b**) (1.91 g, 10 mmol) and bis(4-bromophenyl)fulvene (**20c**) (3.90 g, 10 mmol) were used. Yield: 2.55 g (44%); mp: 219 °C (dec.). Anal. Calcd. for $C_{28}H_{18}Br_2FNO_2$: C, 58.06; H, 3.13; N, 2.42; Found: C, 57.98; H, 3.01; N, 2.31%. IR (KBr): ν_{max} (cm^{-1}) 3067 (CH_{Ar}), 3013 ($CH_{C=C}$), 1774, 1709 (C=O), 1510, 1487 (C=C_{Ar}), 1384, 1182 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.55–6.89 (m, 12H, Ar–H), 6.48 (s, 2H, HC=CH), 3.97 (s, 2H, H-6), 3.56 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 175.2 (C=O), 162.3 (d, C-1, $^1J_{CF}$ = −249.5 Hz), 152.2 (C-7), 138.0 (C-9), 135.0 (HC=CH), 131.6 (C-10), 130.9 (C-11), 128.3 (C-3), 127.5 (C-4), 121.9, 121.8 (C-8, C12), 116.2 (d, C-2, $^2J_{CF}$ = 22.9 Hz), 46.7 (C-6), 44.7 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −112.7 (m, F-1). MS (ESI) *m/z*: 580 $[M+H]^+$ 100%.

4.2.15. *N-(3,5-Difluorophenyl)-7-[bis(4-bromophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (**15**)*

N-(3,5-Difluorophenyl)maleimide (**19c**) (2.09 g, 10 mmol) and bis (4-bromophenyl)fulvene (**20c**) (3.90 g, 10 mmol) were used. Yield: 4.30 g (72%); mp: 229–230 °C (dec.). Anal. Calcd. for $C_{28}H_{17}Br_2F_2NO_2$: C, 56.31; H, 2.87; N, 2.35; Found: C, 56.35; H, 2.90; N, 2.24%. IR (KBr): ν_{max} (cm^{-1}) 3094 (CH_{Ar}), 1775, 1714 (C=O), 1607, 1488 (C=C_{Ar}), 1393, 1171 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.49 (m, 4H, Ar–H), 6.79–6.99 (m, 7H, Ar–H), 6.49 (s, 2H, HC=CH), 3.98 (s, 2H, H-6), 3.58 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 174.5 (C=O), 162.8 (d, C-2, $^1J_{CF}$ = −250.5 Hz), 151.9 (C-7), 138.2 (C-9), 135.1 (HC=CH), 133.5 (t, C-4, $^2J_{CF}$ = 12.7 Hz), 131.6 (C-10), 130.9 (C-11), 122.1, 121.8 (C-8, C-12), 110.0 (d, C-3, $^2J_{CF}$ = 27.9 Hz), 104.3 (t, C-1, $^2J_{CF}$ = 25.2 Hz), 46.8 (C-6), 44.6 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −108.3 (1F, F-2, m). MS (ESI) *m/z*: 598 $[M+H]^+$ 100%.

4.2.16. *N-(2,6-Difluorophenyl)-7-[bis(4-bromophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (**16**)*

N-(2,6-Difluorophenyl)maleimide (**19d**) (2.09 g, 10 mmol) and bis(4-bromophenyl)fulvene (**20c**) (3.90 g, 10 mmol) were used. Yield: 2.75 g (46%); mp: 235–236 °C (dec.). Anal. Calcd. for $C_{28}H_{17}Br_2F_2NO_2$: C, 56.31; H, 2.87; N, 2.35; Found: C, 56.45; H, 2.92; N, 2.22%. IR (KBr): ν_{max} (cm^{-1}) 3079 (CH_{Ar}), 3022 ($CH_{C=C}$), 1784, 1719 (C=O), 1596, 1505 (C=C_{Ar}), 1369, 1168 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.48–7.46 (m, 5H, Ar–H), 7.01–6.94 (m, 6H, Ar–H), 6.49 (s, 2H, HC=CH), 3.97 (s, 2H, H-6), 3.66 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 173.7 (C=O), 158.2 (d, C-3, $^1J_{CF}$ = −256.5 Hz), 151.1 (C-7), 138.3 (C-9), 135.1 (HC=CH), 131.5 (C-10), 131.1 (C-1), 130.9 (C-11), 122.0, 121.7 (C-8, C-12), 112.1 (d, C-2, $^2J_{CF}$ = 19.6 Hz), 110.0 (t, C-4, $^2J_{CF}$ = 17.6 Hz), 46.5 (C-6), 45.4 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −115.5 (m, F-3-syn), −117.7 (m, F-3-anti). MS (ESI) *m/z*: 598 $[M+H]^+$ 100%.

4.2.17. *N-(2,4,6-Trifluorophenyl)-7-[bis(4-bromophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (**17**)*

N-(2,4,6-Trifluorophenyl)maleimide (**19e**) (2.27 g, 10 mmol) and bis(4-bromophenyl)fulvene (**20c**) (3.90 g, 10 mmol) were used. Yield: 3.60 g (59%); mp: 238–239 °C (dec.). Anal. Calcd. for $C_{28}H_{16}Br_2F_3NO_2$: C, 54.66; H, 2.62; N, 2.28; Found: C, 54.76; H, 2.67; N, 2.29%. IR (KBr): ν_{max} (cm^{-1}) 3079 (CH_{Ar}), 3022 ($CH_{C=C}$), 1782, 1725 (C=O), 1609, 1516, 1488 (C=C_{Ar}), 1391, 1172 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.48–7.46 (m, 4H, Ar–H), 6.90–6.79 (m, 6H, Ar–H), 6.48 (s, 2H, HC=CH), 3.96 (s, 2H, H-6), 3.65 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 173.6 (C=O), 163.0 (d, C-1, $^1J_{CF}$ = −253.5 Hz), 158.6 (d, C-3, $^1J_{CF}$ = −256.5 Hz), 152.0 (C-7), 138.3 (C-9), 135.1 (HC=CH), 131.6 (C-10), 130.9 (C-11), 122.2, 121.8 (C-8, C-12), 105.8 (t, C-4, $^2J_{CF}$ = 11.5 Hz), 101.4 (t, C-2, $^2J_{CF}$ = 27.2 Hz), 46.6 (C-6), 45.4 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −104.7 (m, F-1), −112.2 (m, F-3-syn), −114.2 (m, F-3-anti). MS (ESI) *m/z*: 616 $[M+H]^+$ 100%.

4.2.18. *N-(2,3,4,5,6-Pentafluorophenyl)-7-[bis(4-bromophenyl)methylidene]bicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (**18**)*

N-(2,3,4,5,6-Pentafluorophenyl)maleimide (**19f**) (2.63 g, 10 mmol) and bis(4-bromophenyl)fulvene (**20c**) (3.90 g, 10 mmol) were used. Yield: 3.10 g (48%); mp: 237 °C (dec.). Anal. Calcd. for $C_{28}H_{14}Br_2F_5NO_2$: C, 51.64; H, 2.17; N, 2.15; Found: C, 51.84; H, 2.21; N, 2.16%. IR (KBr): ν_{max} (cm^{-1}) 3048 (CH_{Ar}), 3022 ($CH_{C=C}$), 1796, 1729 (C=O), 1517, 1487 (C=C_{Ar}), 1359, 1168 (C–N–C). ^1H NMR ($CDCl_3$): δ_H 7.48 (m, 4H, H-11), 6.95 (m, 4H, H-10), 6.49 (s, 2H, HC=CH), 3.98 (s, 2H, H-6), 3.69 (s, 2H, H-5); ^{13}C NMR ($CDCl_3$): δ_C 172.9 (C=O), 151.6 (C-7), 143.7 (d, C-3, $^1J_{CF}$ = −250.4 Hz), 142.2 (d, C-1, $^1J_{CF}$ = −258.3 Hz), 137.9 (d, C-2, $^1J_{CF}$ = −256.5 Hz), 138.2 (C-9), 135.3 (HC=CH), 131.7 (C-10), 130.9 (C-11), 122.5, 121.9 (C-8, C-12), 106.9 (C-4), 46.7 (C-6), 45.6 (C-5); ^{19}F NMR ($CDCl_3$): δ_F −141.6 (m, F-3-syn), −143.6 (m, F-3-anti), −151.4 (m, F-2), −161.3 (m, F-1). MS (ESI) *m/z*: 652 $[M+H]^+$ 100%.

4.3. *X-ray structure determination*

Single crystals of the reported compounds were obtained by isothermal evaporation or cooling of a saturated solution from acetone or benzene. All crystals were measured on a Bruker Kappa Apex II using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection: SMART; cell refinement: SMART; data reduction: SAINT [39]. Preliminary structure models were derived by Direct Methods [40] and were refined by full-matrix least squares calculation based on *F*2 for all reflections [41]. All non-hydrogen atoms were refined anisotropically. Compounds **13**, **14**·C_6H_6, **17**, and **18** were scaled in multi-scan-mode using SADABS [42]. The hydrogen atoms were included in the models in calculated positions. For the compounds **6** and **14**·C_6H_6, a special treatment is required due to structural disorder.

The structure of compound **6**, involves two independent disorders and hence the molecule was refined in two positions: (1) the main position of the imide unit and pentafluoro substituted phenyl group with 81.4%, and an additional but independent position of the methylidene bonded phenyl ring with 35.1%; (2) the secondary position of the imide unit and fluorinated phenyl ring with 18.6%, and the independent position of the methylidene bounded phenyl ring with 64.9%.

Compound **14** was also refined in two positions: the main position with 84.2% and the secondary position with 15.8%. Due to the remaining electron density and the shape of the ellipsoids of the benzene it can be concluded that the benzene molecule itself is probably disordered four times since it has more than two adjacent molecules existing in two different shapes in space. On the other hand, a continuous transition and an electron density maximum cannot be detected. Therefore, a refinement of all possible positions of the guest molecule was omitted.

All crystal data and experimental parameters are summarized in Table S1 (SI). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the

Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 740955–740970 Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2009.11.013.

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