Electronic Supplementary Information

On the supramolecular outcomes of fluorination of cyclohexane-5-spirohydantoin derivatives

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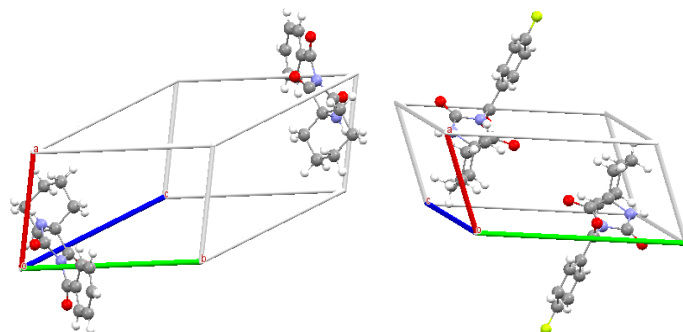
Fig. S1 Representation of the unit cells of **1** (left) and **2** (right).

Table S1 Selected bond lengths (Å) and angles (°) in the investigated compounds.

	1	2
N1–C2	1.330(2)	1.330(2)
C2–N3	1.419(3)	1.396(3)
N3–C4	1.398(2)	1.377(3)
C4–C5	1.514(2)	1.520(2)
C5–N1	1.452(2)	1.452(3)
N3–C11	1.434(2)	1.459(2)
C11–C12	1.488(3)	1.454(2)
C2–O1	1.213(2)	1.221(3)
C4–O2	1.201(2)	1.205(3)
C11–O3	1.202(3)	1.195(3)
C2–N1–C5	114.2(2)	113.8(2)
O1–C2–N1	128.8(2)	128.9(2)
O1–C2–N3	124.1(2)	123.8(2)
N1–C2–N3	107.1(2)	107.3(2)
C2–N3–C4	110.2(2)	111.1(2)
O2–C4–N3	125.9(2)	125.7(2)
O2–C4–C5	126.9(2)	127.2(2)
N3–C4–C5	107.2(2)	107.1(2)
N1–C5–C4	101.3(2)	100.6(2)
N3–C11–C12	118.5(2)	117.2(2)
N3–C11–O3	118.7(2)	117.0(2)
C12–C11–O3	122.8(2)	125.8(3)
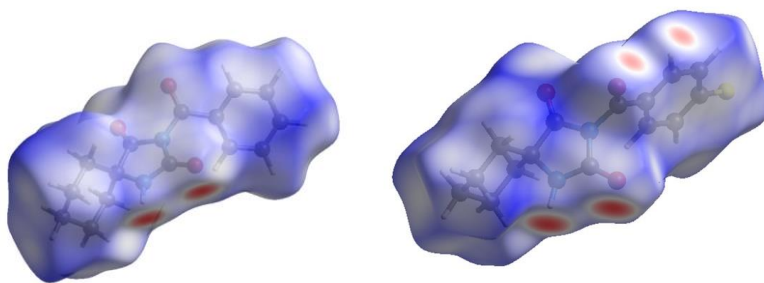
Fig. S2 Views of Hirshfeld surfaces mapped over d_{norm} for **1** (left) and **2** (right).

1   **1** *H···H* 50.9%   **1** *O···H* 28.8%   **1** *C···H* 14.0%
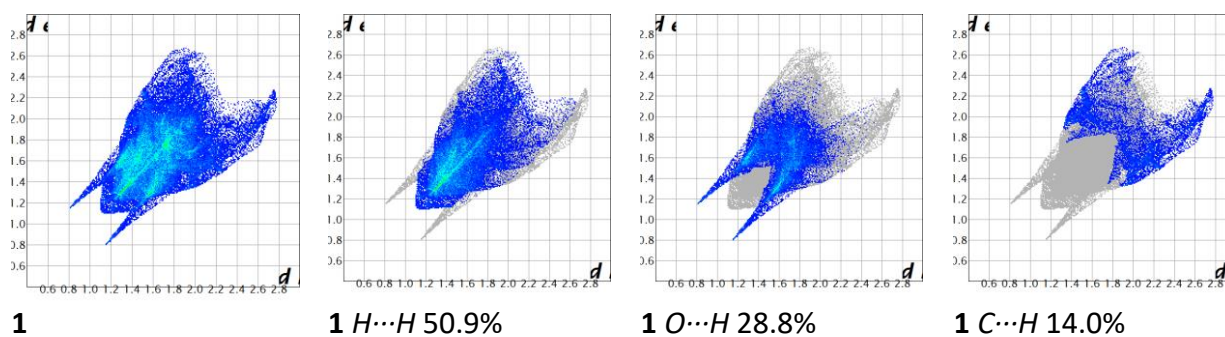
Fig. S3 Fingerprint plot of **1** and plots decomposed into contributions from specific reciprocal intermolecular atom–atom contacts. For each plot, the grey shadow is an outline of the complete fingerprint plot.

2   **2** *H···H* 34.6%   **2** *O···H* 33.3%   **2** *C···H* 14.0%

2 *F···H* 12.6%
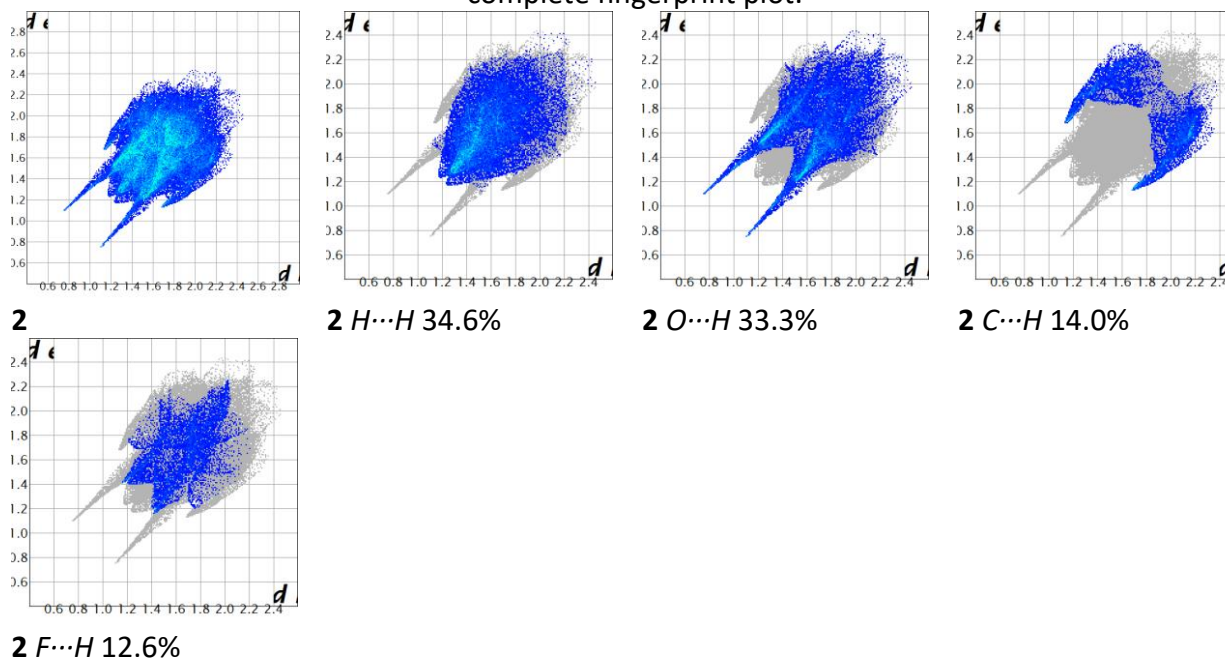
Fig. S4 Fingerprint plot of **2** and plots decomposed into contributions from specific reciprocal intermolecular atom–atom contacts. For each plot, the grey shadow is an outline of the complete fingerprint plot.
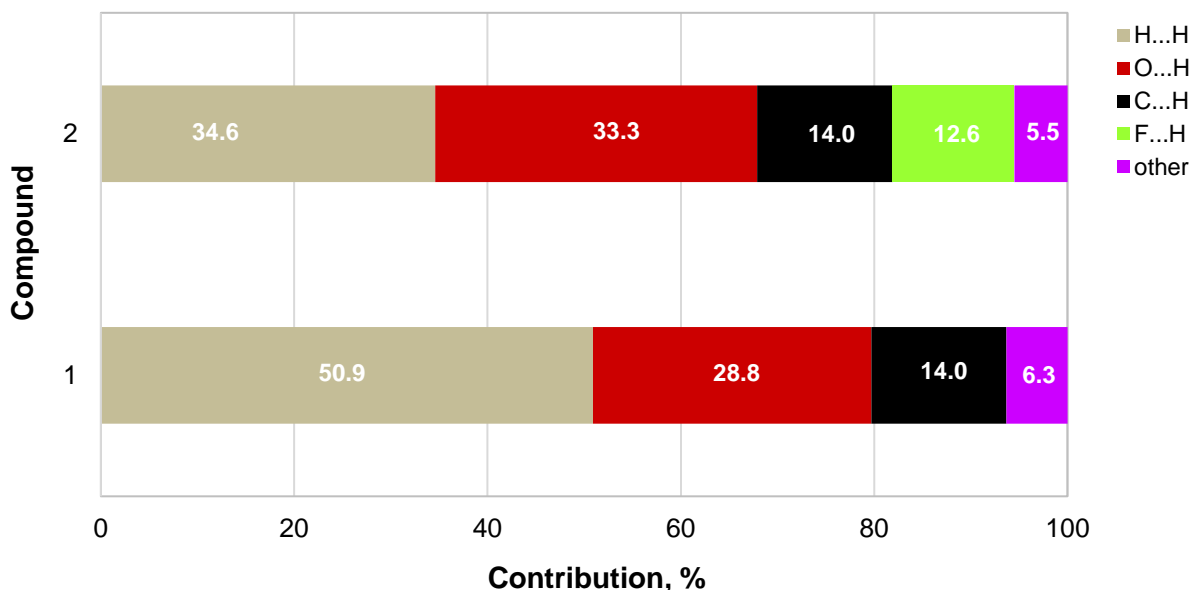
Fig. S5 Relative contribution of intermolecular atom–atom contacts to the Hirshfeld surface area.

ESI3. Energy frameworks

Table S2 Lattice energies contributions of electronic, polarization, dispersion and repulsion energies using PIXEL (kcal/mol).

Compound	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}	Level of theory
1	−15.18	−6.24	−32.77	20.91	−33.27	MP2/6-31(d,p)
	−15.37	−6.33	−32.70	20.17	−34.23	B3LYP/6-31(d,p)
2	−17.76	−6.36	−30.66	20.53	−34.25	MP2/6-31(d,p)
	−17.97	−6.41	−30.59	20.00	−34.99	B3LYP/6-31(d,p)

Table S3 *Crystal Explorer* interaction energies (in kcal/mol) of the extracted dimeric motif for **1**, calculated at B3LYP/6-31G(d,p) level of theory.

Motif	R[a]	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}	E_{tot}[b]
H1	6.14	−16.78	−4.61	−7.62	16.13	−17.81	−20.88
H2	4.83	−2.01	−1.15	−11.35	4.09	−10.33	−12.31
H3	6.87	−2.61	−0.69	−11.52	6.19	−9.51	−10.54
H4	8.24	−3.92	−1.36	−4.49	2.65	−7.41	−7.99
H5	6.31	−1.82	−1.24	−8.37	5.38	−6.79	−12.31
H6	12.19	−0.10	−0.14	−2.37	1.08	−1.58	−1.58
H7	13.58	−0.07	−0.07	−1.72	0.91	−1.05	−1.32
H8	13.57	0.31	−0.07	−1.58	0.67	−0.72	−0.8

[a] Distance between the centres of mass in Å.
[b] Interaction energies of dimeric motif calculated at TPSSh-D3/def2TZVP level of theory.

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Table S4 *Crystal Explorer* interaction energies (in kcal/mol) of the extracted dimeric motifs for **2**, calculated at B3LYP/6-31G(d,p) level of theory.

Motif	R^a	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}	$E_{tot}{}^b$
F1	7.24	−21.13	−5.62	−6.05	19.79	−19.55	−21.12
F2	5.24	−3.13	−0.86	−11.07	5.11	−10.40	−11.73
F7	8.01	−2.87	−0.98	−6.88	2.70	−8.08	−9.09
F3	8.53	−2.89	−0.76	−7.65	4.02	−7.82	−9.03
F6	6.00	−0.62	−0.91	−7.60	2.87	−6.19	−7.31
F9	8.76	−4.35	−0.91	−2.84	4.71	−4.85	−5.04
F8	7.24	−0.33	−0.29	−4.54	2.63	−2.92	−2.74
F5	14.07	−0.29	−0.05	−1.63	0.91	−1.20	−1.31
F4	13.77	0.24	−0.07	−2.27	1.10	−1.10	−1.27
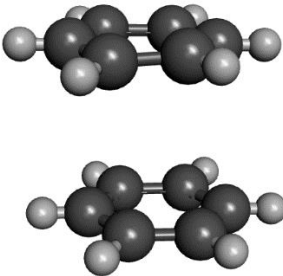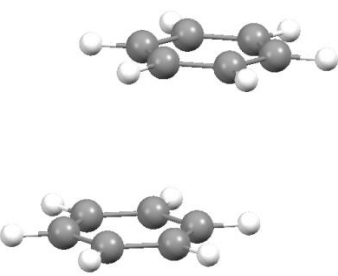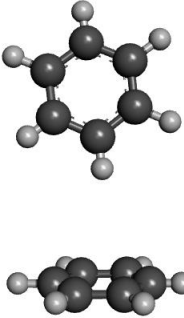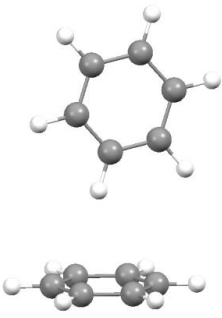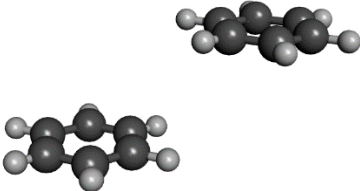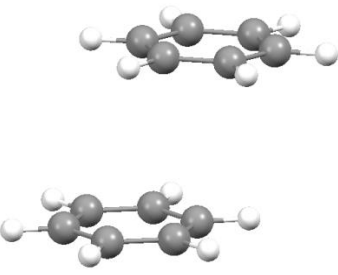
^{a} Distance between the centres of mass in Å.
^{b} Interaction energies of dimeric motif calculated at TPSSh-D3/def2TZVP level of theory.

ESI4. Contacts of the individual cyclic fragments in the crystal structure of 1
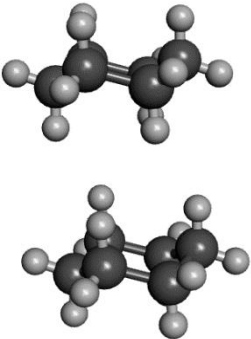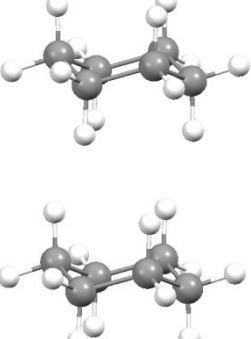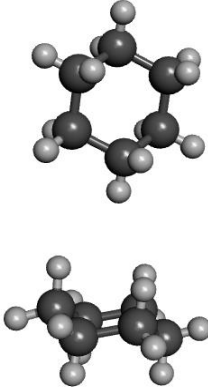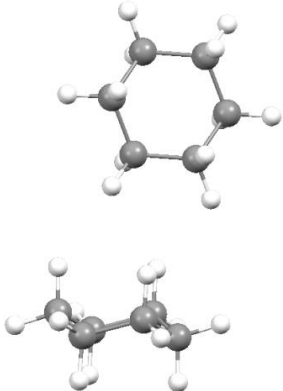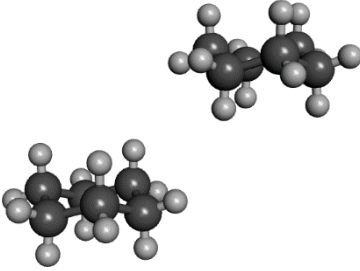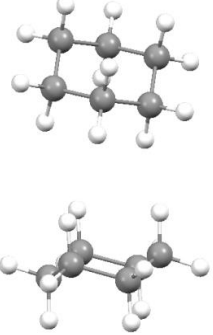
Table S5 Analysis of intermolecular contacts of the cyclic fragments, which are present in **1**.

	Hydantoin	Cyclohexane	Benzene
Hydantoin	H1, H8	2×H2, H7	2×H3
Cyclohexane	2×H2, H7	H6	H4, H5, H7, 2×H8
Benzene	2×H3	H4, H5, H7, 2×H8	H3, H7
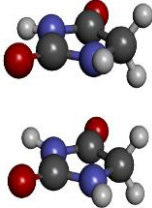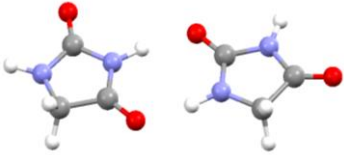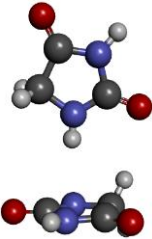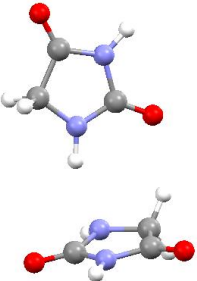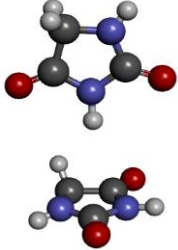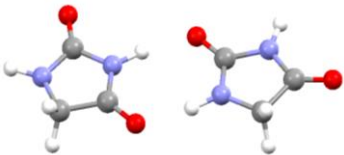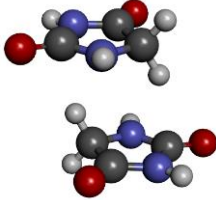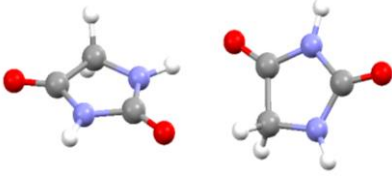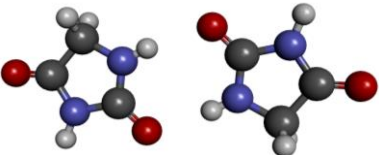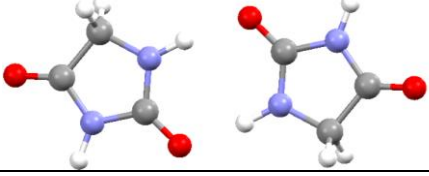
Table S6 The results of calculations on the benzene–benzene model systems.

Starting structure	Optimized structure
Face-to-face geometry	Stacking geometry −2.66 kcal/mol
T-shaped geometry	T-shaped geometry −2.86 kcal/mol
Displaced geometry with large offset	Stacking geometry −2.66 kcal/mol

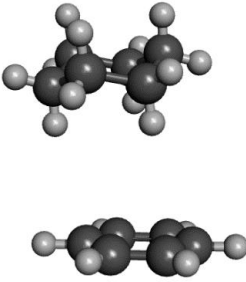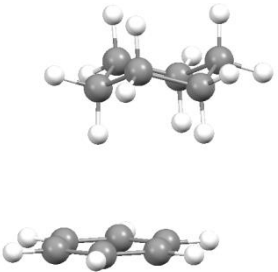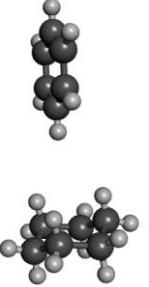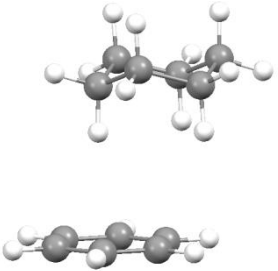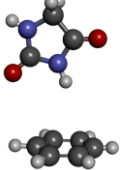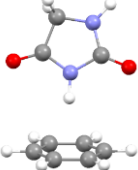**Table S7** The results of calculations on the cyclohexane–cyclohexane model systems.
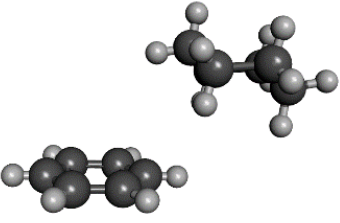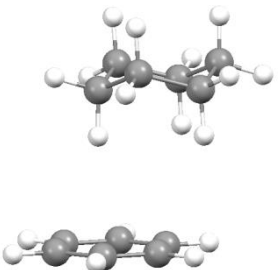
Starting structure	Optimized structure
Face-to-face geometry	Face-to-face geometry −3.02 kcal/mol
T-shaped geometry	T-shape geometry −2.34 kcal/mol
Displaced geometry with large offset	Tilted geometry −2.71 kcal/mol

Table S8 The results of calculations on the hydantoin–hydantoin model systems.
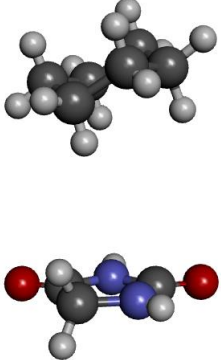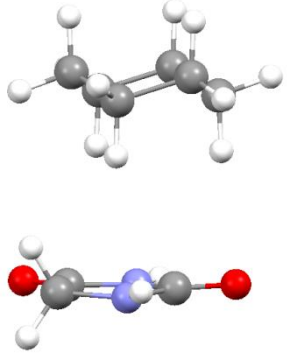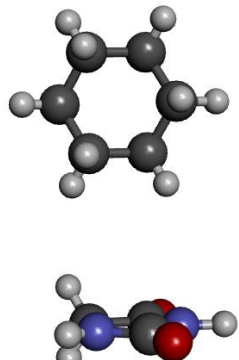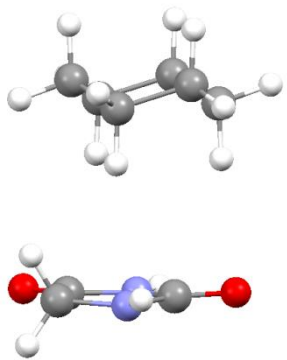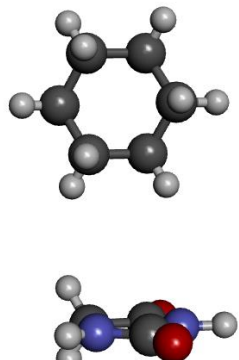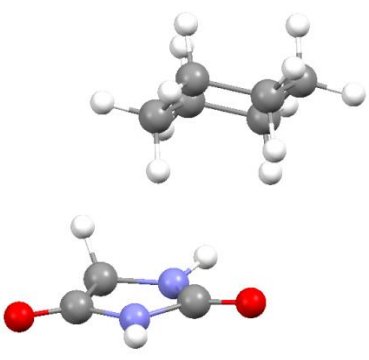
Starting structure	Optimized structure
Face-to-face geometry	Planar geometry −16.15 kcal/mol
T-shape geometry 1	T-shape geometry −6.88 kcal/mol
T-shape geometry 2	Planar geometry −16.15 kcal/mol
Displaced geometry	Planar geometry −11.20 kcal/mol
Planar geometry	Planar geometry −17.83 kcal/mol
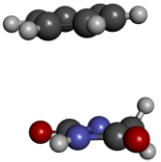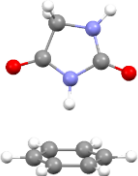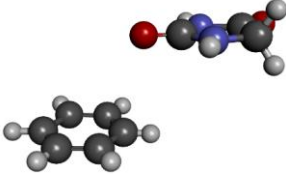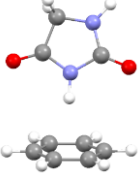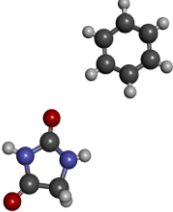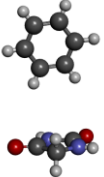
Table S9 The results of calculations on the cyclohexane–benzene model systems.

Starting structure	Optimized structure
Face-to-face geometry	Displaced geometry −3.43 kcal/mol
T-shaped geometry	Displaced geometry −3.49 kcal/mol
Displaced geometry with large offset	Displaced geometry −3.47 kcal/mol

Table S10 The results of calculations on the cyclohexane–hydantoin model systems.

Starting structure	Optimized structure
Face-to-face geometry	Displaced geometry −3.57 kcal/mol
T-shaped geometry 1	Displaced geometry −3.57 kcal/mol
T-shaped geometry 2	Displaced geometry −3.82 kcal/mol

Table S11 The results of calculations on the hydantoin–benzene model systems.

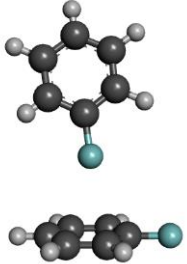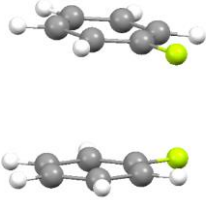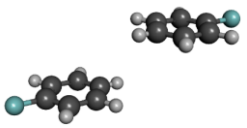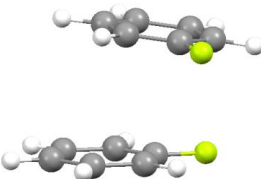| Starting structure	Optimized structure
Face-to-face geometry	T-shaped geometry −5.25 kcal/mol
Displaced geometry	T-shaped geometry −5.37 kcal/mol
Planar geometry	T-shaped geometry −6.36 kcal/mol
T-shaped geometry	T-shaped geometry −5.71 kcal/mol
T-shaped geometry	T-shaped geometry −6.36 kcal/mol
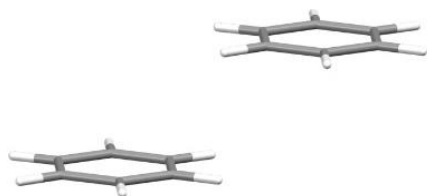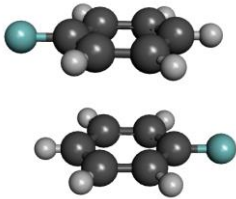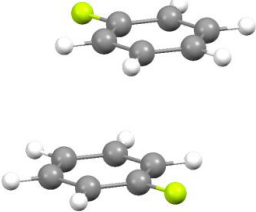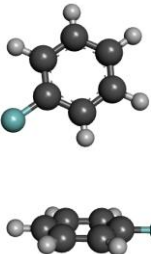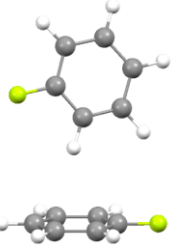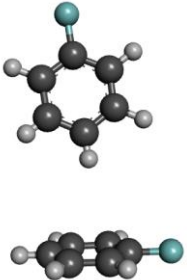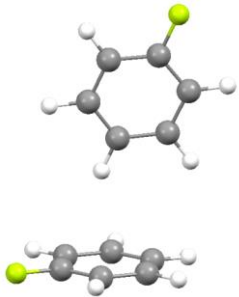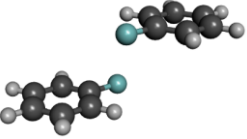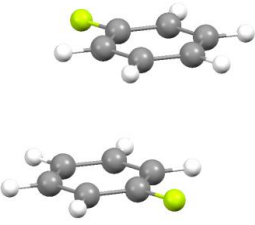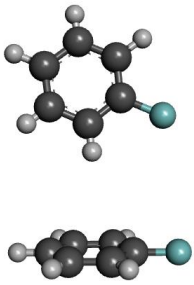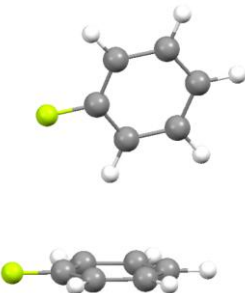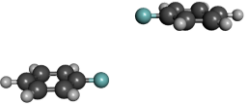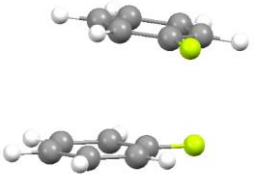
Fig. S6 The most stable parallel geometry of the benzene dimer without overlap of the rings, corresponding to parallel interaction at a large offset with interaction energy of –1.98 kcal/mol.[S1]

ESI5. Contacts of the individual cyclic fragments in the crystal structure of 2

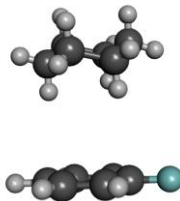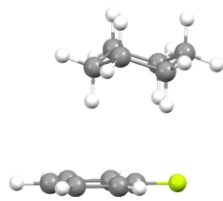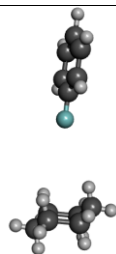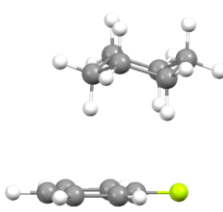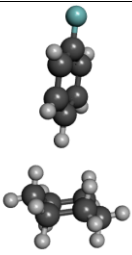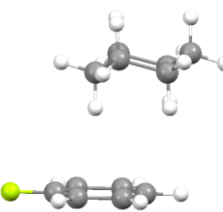**Table S12** Analysis of intermolecular contacts of the cyclic fragments, which are present in **2**.

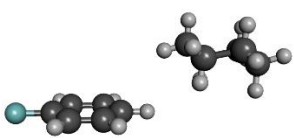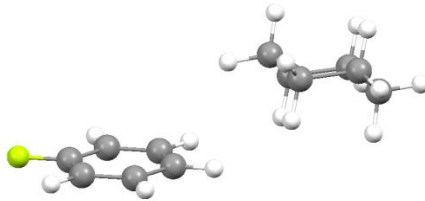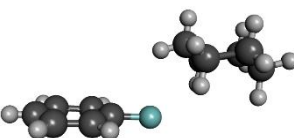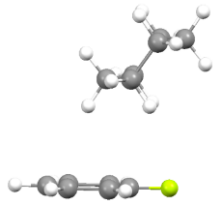|	Hydantoin	Cyclohexane	Fluorobenzene
Hydantoin	F1	2xF2, F6, 2xF7	2×F3, F6
Cyclohexane	2×F2, F6, 2×F7	F4	2×F2, F5, 2×F7, 2×F8
Fluorobenzene	2×F3, F6	2×F2, F5, 2×F7, 2×F8	F3, F6, F9

ESI6. Quantum chemical calculations on the model cyclic compounds present as fragments in 2
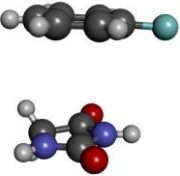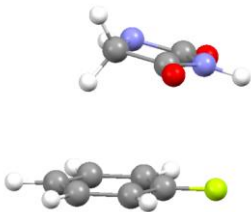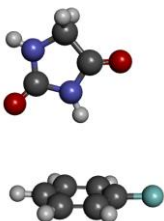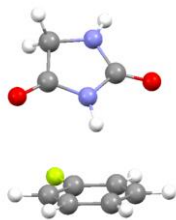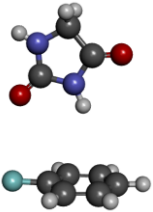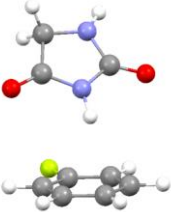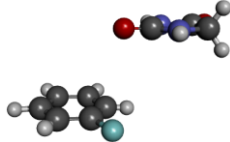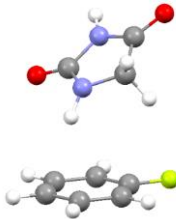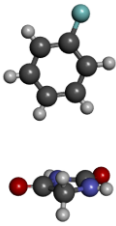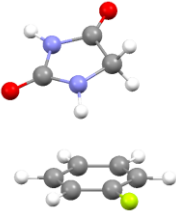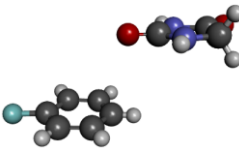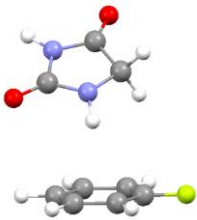
Table S13 The results of calculations on the fluorobenzene–fluorobenzene model systems.

Starting structure	Optimized structure	Starting Structure	Optimized structure
Face-to-face geometry	Displaced geometry −3.68 kcal/mol	T-shaped geometry 4	T-shaped geometry −3.24 kcal/mol
T-shaped geometry 1	T-shaped geometry −2.83 kcal/mol	Displaced geometry	Displaced geometry −3.68 kcal/mol
T-shaped geometry 2	T-shaped geometry −2.80 kcal/mol	Displaced geometry with large offset 1	Displaced geometry −3.36 kcal/mol
T-shape geometry 2	Displaced geometry −3.57 kcal/mol	Displaced geometry with large offset 2	Displaced geometry −3.41 kcal/mol

Table S14 The results of calculations on the cyclohexane–fluorobenzene model systems.

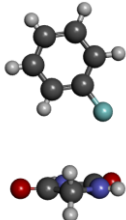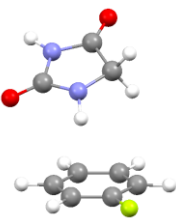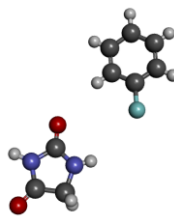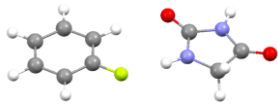| Starting structure	Optimized structure
Face-to-face geometry	Displaced geometry −3.69 kcal/mol
T-shaped geometry 1	Displaced geometry −3.60 kcal/mol
T-shaped geometry 2	Displaced geometry −3.41 kcal/mol
Displaced geometry 1	Displaced geometry with large offset −2.13 kcal/mol
Displaced geometry 2	Displaced geometry −3.28 kcal/mol

Table S15 The results of calculations on the hydantoin–fluorobenzene model systems.

Starting structure	Optimized structure	Starting Structure	Optimized structure
Face-to-face geometry	Displaced geometry –6.10 kcal/mol	T-shaped geometry 4	T-shaped geometry –5.78 kcal/mol
T-shaped geometry 1	T-shaped geometry –5.78 kcal/mol	Displaced geometry 1	T-shaped geometry –5.94 kcal/mol
T-shaped geometry 2	T-shaped geometry –5.74 kcal/mol	Displaced geometry 2	T-shaped geometry –5.57 kcal/mol
T-shaped geometry 2	T-shaped geometry –5.74 kcal/mol	Planar geometry	Planar geometry –5.67 kcal/mol

ESI7. F···F interaction in the crystal structure of 2

$d= 4.26$ Å
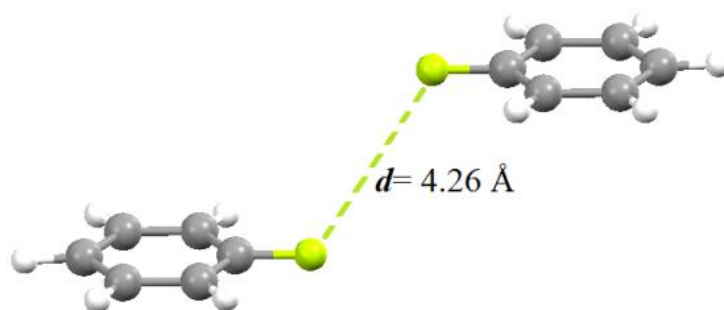
$\Delta E= -0.02$ kcal/mol

Fig. S7 Motif extracted from the crystal structure of **2** involving the F···F interaction with the associated interaction energy.

References

S1   D. B. Ninković, G. V.Janjić, D. Ž. Veljković, D. N. Sredojević and S. D. Zarić, What Are the preferred horizontal displacements in parallel aromatic–aromatic interactions? Significant interactions at large displacements, *ChemPhysChem*, 2011, **12**, 3511.