

Supporting Material for:

Chemistry of 1-fluoro-2,3,4-triphenylcyclobutadiene dimers

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Supporting Materials: Crystal structures have been deposited at the Cambridge Crystallographic Data Center and allocated the deposition numbers CCDC 294075 – 294079. The CIF

Experimental part: Crystals of **3a** prepared in 1959-1960 were used as such. Compounds **5**, **4** and **6** were crystallized from acetone and **9** from benzene. Single-crystal diffraction data for the five crystals were collected on a Bruker AXS Smart Apex CCD diffractometer at 293(2) K. The X-ray generator was operated at 50kV and 35mA using MoK_α radiation. Data was collected with ω scan width of 0.3°. A total of 606 frames were collected in SAINTPLUS¹ and an empirical absorption correction was applied using the package SADABS.² XPREP² was used to determine the space group. The crystal structure was solved by direct methods using SIR92³ and refined by the full-matrix least-squares method using

SHELXL97⁴ present in the program suite WinGx (Version 1.63.04a).⁵ Molecular diagrams were generated using ORTEP-32⁶ and the packing diagrams were generated using CAMERON.⁷ Geometrical calculations were done using PARST95⁸ and PLATON.⁹ Details of data collection and refinement are given in Table S1 and intermolecular interactions in Table S2.

Discussion: The crystals **3a** are triclinic system, space group $P\bar{1}$, with $Z=2$. The overcrowding in the molecule arising from interactions between the rings on the double bonds and the adjacent fluorine substitution renders the central three four-membered rings to adopt a "ladder-like sofa" conformation. The angle between the least-squares planes of the rings C1, C2, C3 and C4 [ring1] and C4, C5, C8 and C1 [ring 2] is $-65.8(1)^\circ$ and that between C4, C5, C8 and C1 [ring 2] and C5, C6, C7, C8 [ring3] is $-65.4(2)^\circ$ respectively, close to the values of the earlier report.¹⁰ The corresponding angle between rings 1 and 3 is $0.7(2)^\circ$. The ORTEP, Figure S1 displays the 30% ellipsoidal probability plot of the molecule. It is interesting that only one C-H... π interaction (Table S2) holds the molecules together in the unit cell as dimers as can be seen in the Figure S2.

Compound **6** is an isomer of **5** and also crystallizes in the space group $P\bar{1}$, with $Z=2$. The ORTEP is shown in Figure S4 and the packing of the molecules in Figure S3. The dimer in this structure is a classical example of a head-to-tail C-H... π interaction as shown in Figure S4. The angle between the two central five-membered rings is $42.8(1)^\circ$. There is a significant increase in the puckering of the rings with the difference in the phenyl-group substitutions mode compared to **5**.

Compound **9** crystallizes in the space group $P\bar{1}$ with a benzene molecule of crystallization. The ORTEP is shown in Figure S4 and the packing of the molecules in the unit cell in Figure S5. The packing has very weak intermolecular C-H... π contacts (Table S2), generating dimeric units held as chains in a direction perpendicular to the dimers. The central three fused rings are not confined to a plane, as is evident from the angles between rings. Thus, C1, C2, C3, C4, C5 and C14 makes an angle of $12.6(7)^\circ$ with C4, C5, C6, C7, C12, while C13: C4, C5, C6, C7, C12 and C13 makes an angle of

8.2(1)° with C7, C8, C9, C10, C11 and C12, which in turn is at an angle of 20.8(3)° with C1, C2, C3, C4, C5 and C14. The array of interacting phenyl groups on the phenanthrene is reasonably responsible for the lack of coplanarity. The benzene molecules in the lattice do not appear to participate in significant intermolecular interactions.

Compound **4** is triclinic, $P\bar{1}$, with $Z=2$ and is an isomer of **3a**. The ORTEP is in Figure 2 and the packing in Figure S6. The molecules are held together as tetrameric units via weak C-H... π interactions. The central five-membered rings are V-shaped with the angle between the planes being 23.2(2)°. Rummery¹¹ has reported that this structure has been determined by X-ray diffraction, but the details have not been published, although near coplanarity of the double bonds was suggested, which is contrary to our findings. The two pentalenone derivatives **5** and **6**, which we report here, are both puckered to the extent of 42.8° and 31.8° respectively. Currently we are carrying out a study of the thermal transformation of **3a** to **4** with the aid of *in situ* high-temperature single-crystal X-ray diffraction studies.

Compound **5** crystallizes in a triclinic system, space group $P\bar{1}$, with $Z=2$. The ORTEP (30% probability) is given in Figure S1 and the packing diagram in Figure S7. There are no significantly strong interactions, except weak C-H... π interactions, which control the crystal packing by generating dimeric units, which in turn produce tetrameric assemblies as shown in Figure S8. The central two five-membered rings generate a V-shaped structure with an angle between the two rings of 31.8(9)°.

References:

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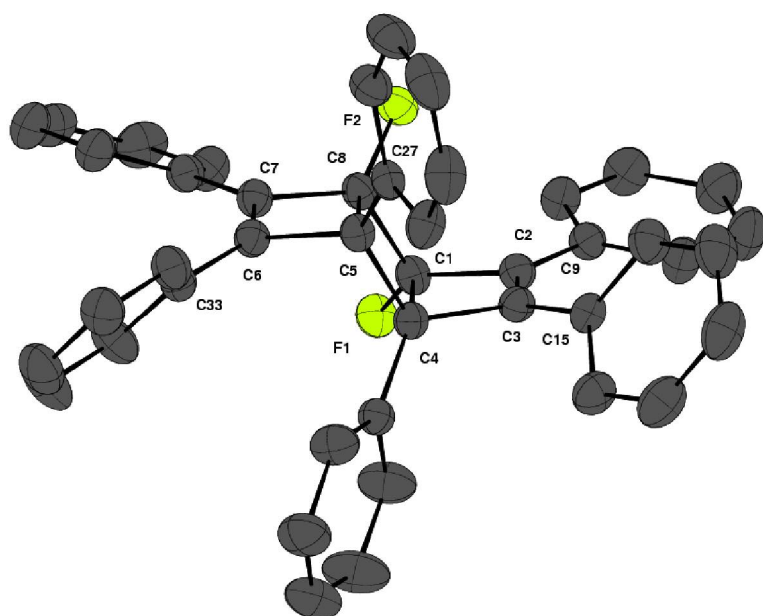


Figure S1. ORTEP of **3a** with 30% probability ellipsoids.

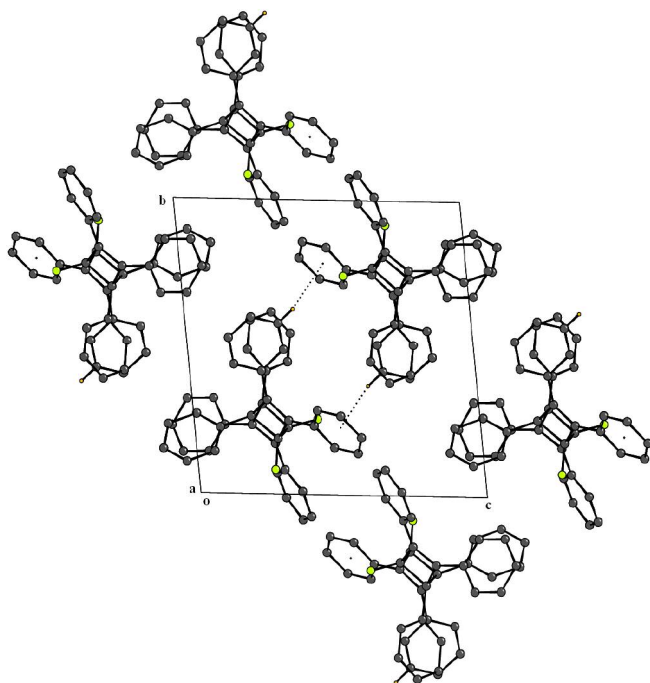


Figure S2. Packing of **3a** crystals viewed down '*a*' axis, with intermolecular C-H... π interactions shown as dotted lines.

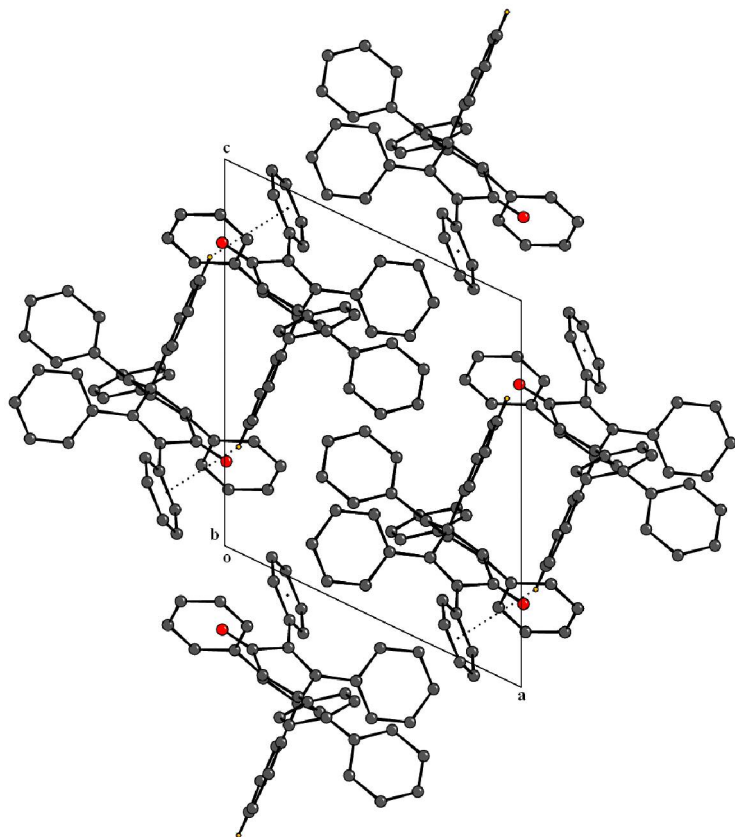


Figure S3. Packing of **6** viewed down '*b*' axis, intermolecular C-H... π interactions.

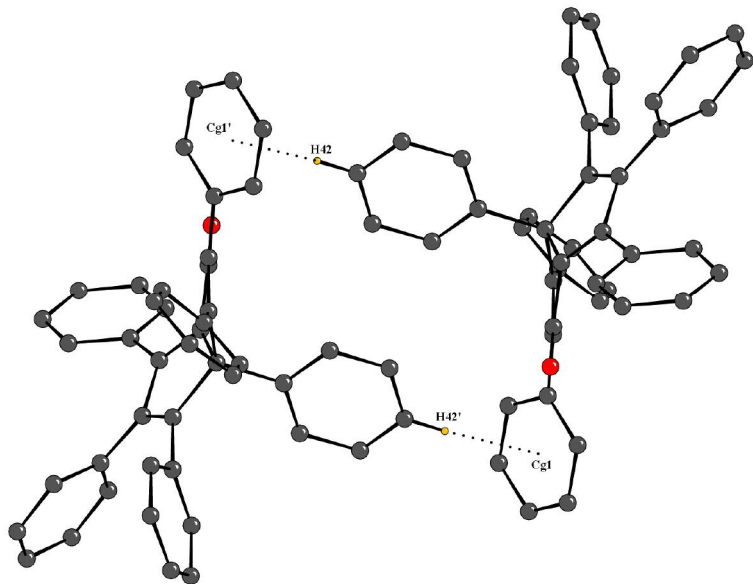


Figure S4. The C-H... π interactions associated with dimer formation across the center of symmetry of **6**.

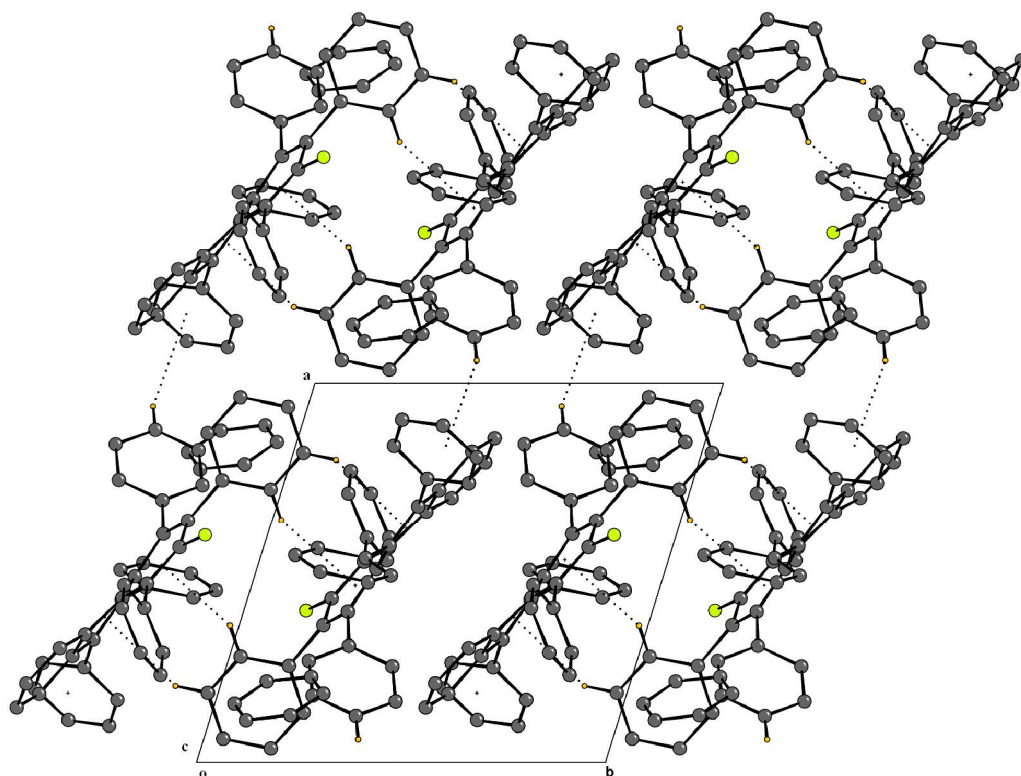


Figure S5. Packing of the molecules of **9** in the crystal lattice, where the C-H... π interactions are shown as dotted lines.

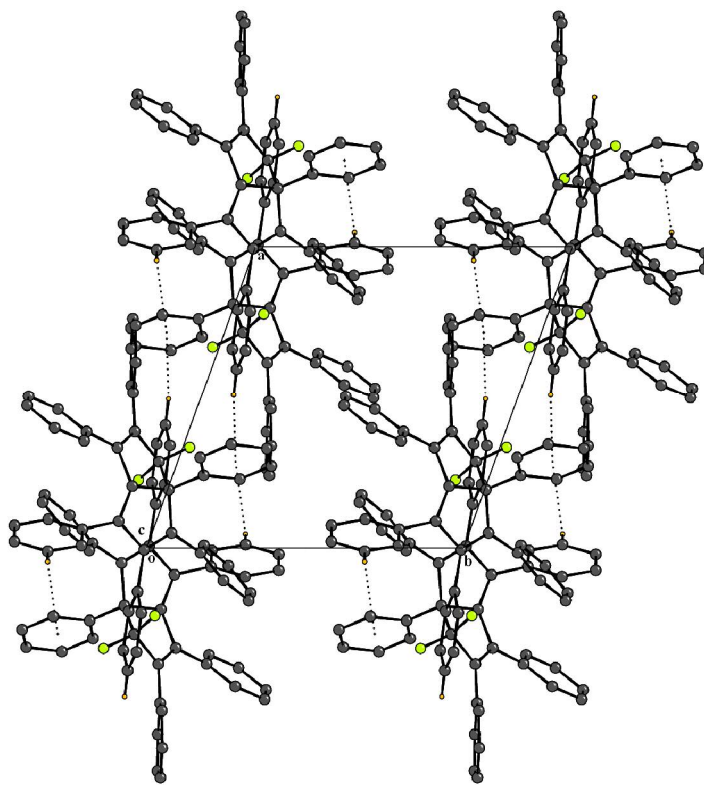


Figure S6. Packing of **4** with tetrameric units forming parallel chains along the “a” axis.

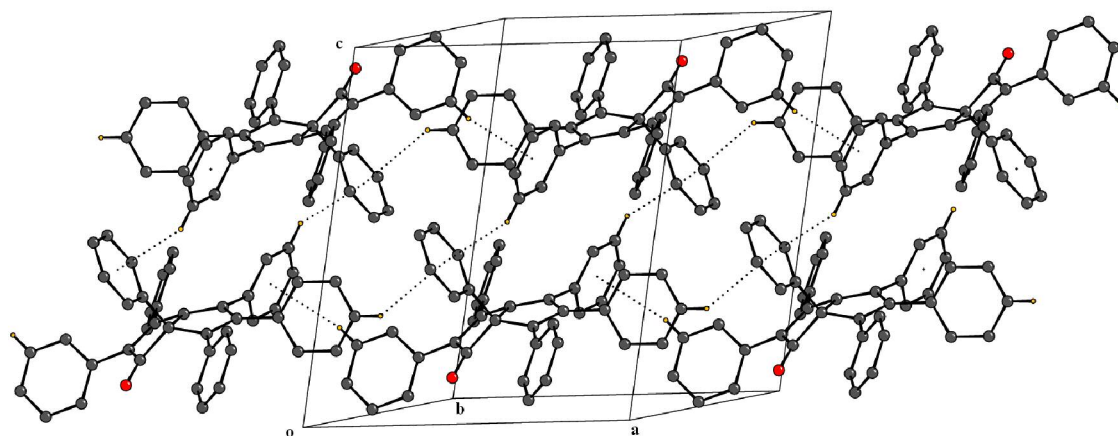


Figure S7. Packing of **5**, intermolecular C-H... π interactions shown as dotted lines.

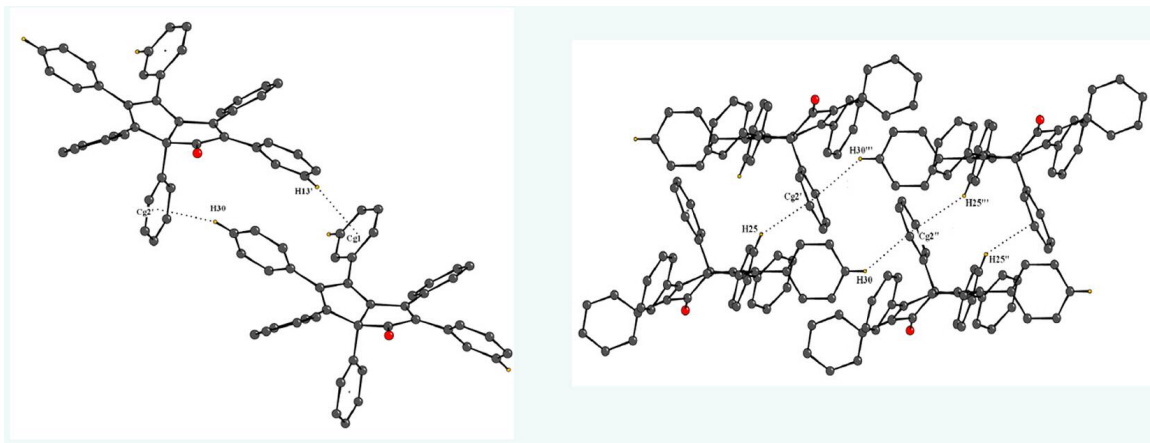


Figure S8. The buildup of dimeric and tetrameric units of **5** as the result of ring contacts

Table S1: Crystal Data and Refinement Results

	3 [‡]	6 [†]	9	4 [‡]	5 [†]
Formula	C ₄₄ H ₃₀ F ₂	C ₄₄ H ₃₀ O	C ₅₀ H ₃₅ F	C ₄₄ H ₃₀ F ₂	C ₄₄ H ₃₀ O
Formula Weight	596.7	574.7	654.8	596.7	574.7
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
a/Å	9.295(4)	11.306(2)	11.248(7)	11.297(2)	11.190(2)
b/Å	13.104(5)	12.280(2)	11.808(7)	11.788(2)	11.733(2)
c/Å	13.543(6)	13.153(2)	14.733(9)	13.350(3)	13.374(2)
α/°	95.980(7)	100.175(2)	76.39(1)	71.565(3)	70.931(3)
β/°	104.223(6)	111.872(3)	83.72(1)	85.639(4)	82.481(3)
γ/°	91.859(7)	103.078(2)	71.79(1)	69.700(3)	70.186(2)
Volume/Å ³	1587.4(3)	1580.4(3)	1805.0(8)	1580.8(3)	1560.9(2)
Space Group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
Z	2	2	2	2	2
Density/gcm ⁻³	1.25	1.21	1.20	1.25	1.22
Radiation	MoK _α	MoK _α	MoK _α	MoK _α	MoK _α
Temperature/K	293(2)	293(2)	293(2)	293(2)	293(2)
μ/mm ⁻¹	0.079	0.071	0.072	0.079	0.071
θ _{min, max} /°	1.6, 25.4	1.7, 25.4	1.9, 25.4	1.6, 25.4	1.9, 25.4

Unique Reflections	5716	5739	6512	5716	5670
No. of parameters	415	406	460	415	406
R, R _w	0.064, 0.235	0.079, 0.141	0.061, 0.108	0.068, 0.132	0.062, 0.130
$\Delta\rho_{\min}$, $\rho_{\max}/e\text{\AA}^{-3}$	-0.189, 0.309	-0.149, 0.178	-0.142, 0.163	-0.157, 0.176	-0.146, 0.573
Goof	1.123	1.164	0.994	1.163	1.025

† Isomers; ‡ Isomers

Table S2: Intermolecular C-H... π interactions

Compound	D-B...A	D...A/Å	B...A/Å	D- B...A/ ^o	Symmetry
3	C17- H17...Cg1	3.638(5)	2.88	140.0	- x, 1 - y, 1 - z
6	C42- H42...Cg1	3.804(4)	3.07	137.5	2 - x, - y, 1 - z
9	C19- H19...Cg1	3.593(4)	2.77	147.6	1 - x, 2 - y, - z
	C20- H20...Cg2	3.705(3)	2.87	149.6	1 - x, 2 - y, - z
	C24- H24...Cg3	3.826(3)	3.02	146.3	1 + x, y, z
4	C25- H25...Cg1	3.560(4)	2.81	138.0	- x, 2 - y, - z
	C30- H30...Cg1	3.721(3)	2.94	142.2	- 1 + x, y, z
5	C13- H13...Cg1	3.782(4)	2.88	164.5	-1 + x, y, z
	C25- H25...Cg2	3.582(4)	2.82	140.3	1 - x, 1 - y, 1 - z

	C30- H30...Cg2	3.771(4)	2.92	142.3	1 + x, y, z
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