Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unusual bonding modes of perfluorobenzene in its polymeric (dimeric, trimeric and tetrameric) forms: Negative fluorines interacting cooperatively with negative fluorines

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Supplementary Information

Fig. S1: The crystal of perfluoromethane CF_4 (ref code TFMETH03), [1] obtained from Cambridge Structure Database (CSD).[2] Selected F···F intermolecular bond distances are given in units of Å.

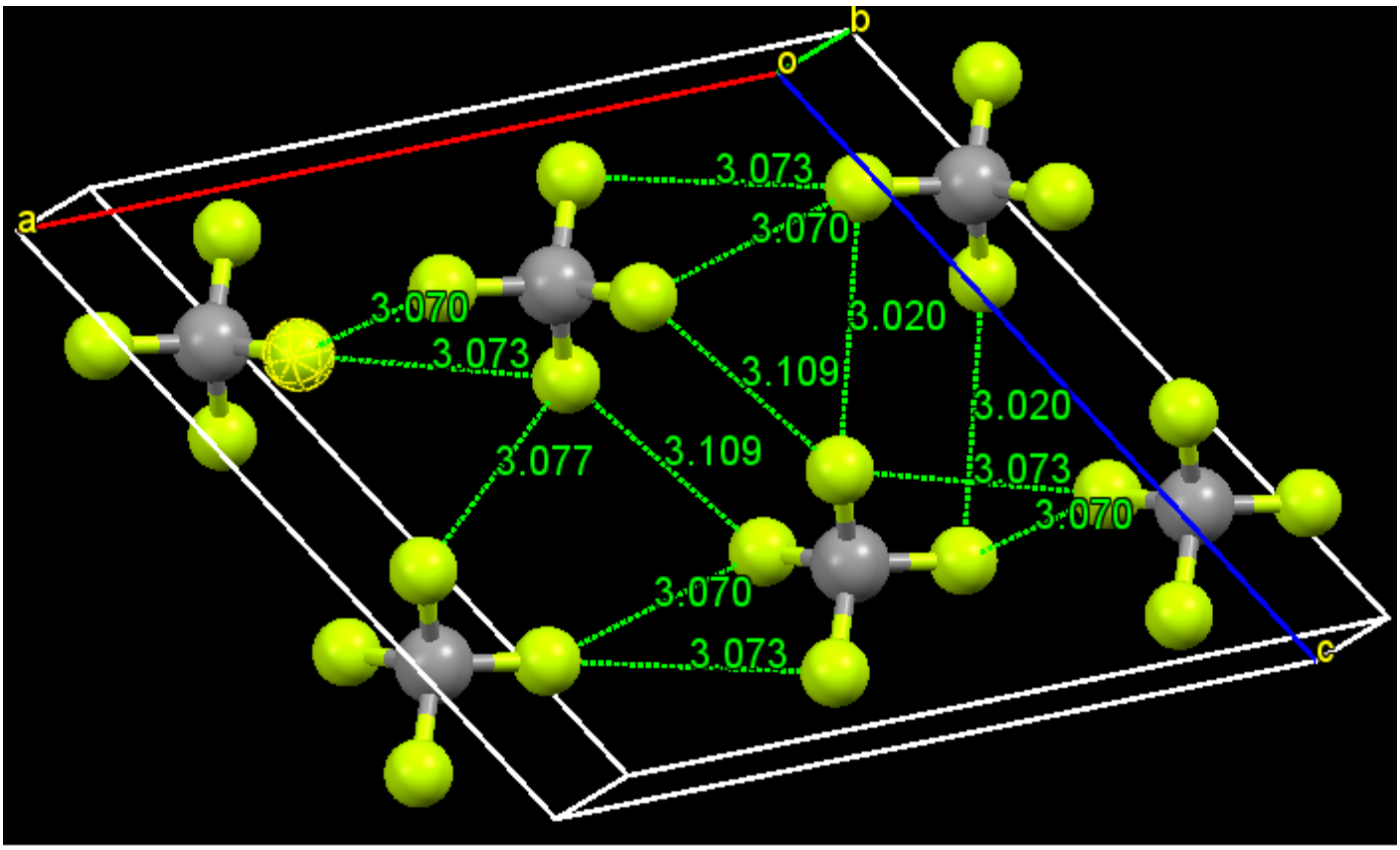

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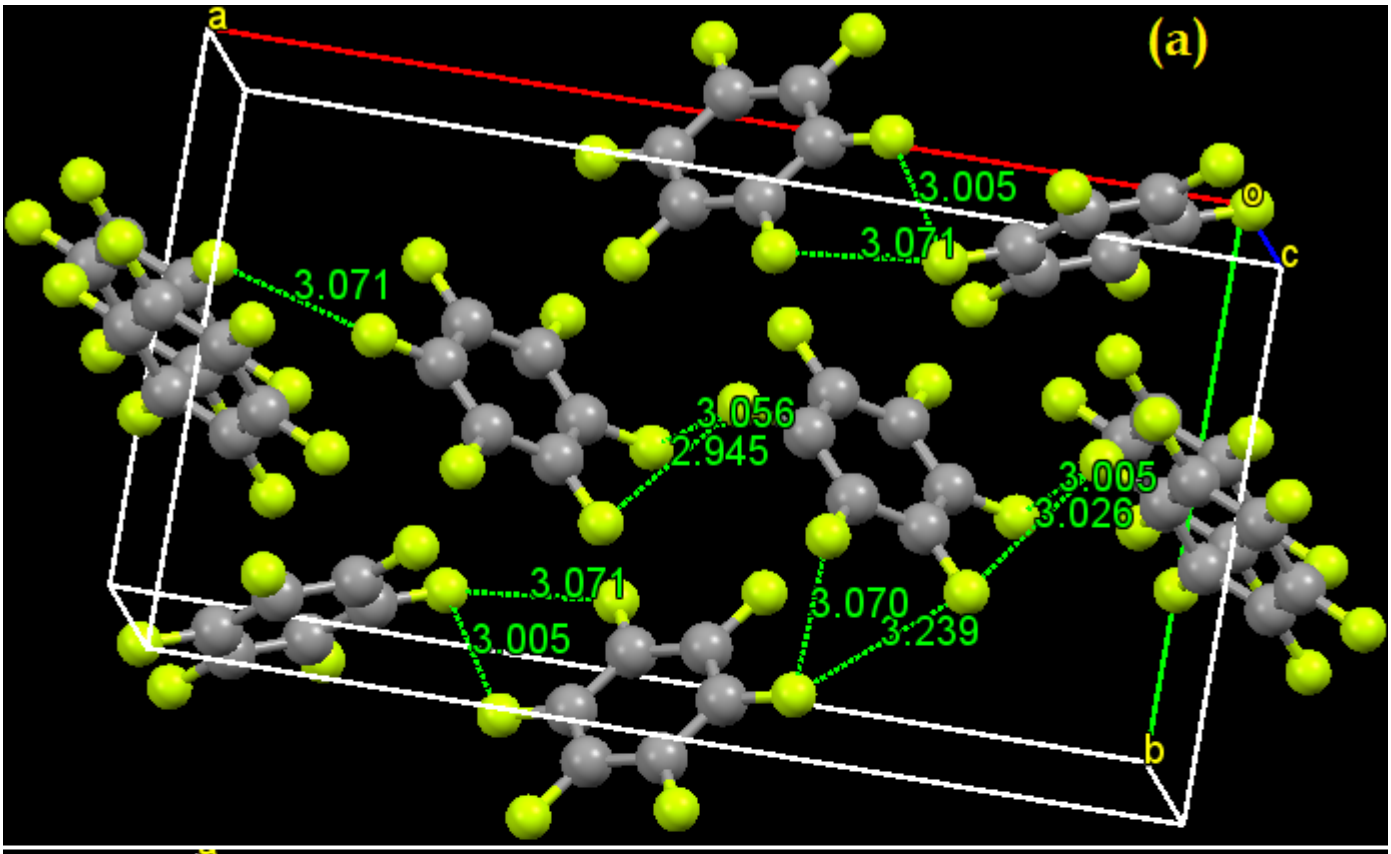
Fig. S2: The crystal of perfluorobenzene C_6F_6 (refcode HFBENZ11),[3] obtained from Cambridge Structure Database (CSD).[2] Both ball and stick (a), and crapped sticks (b) models are illustrated. Selected F···F intermolecular bond distances are given in units of Å.



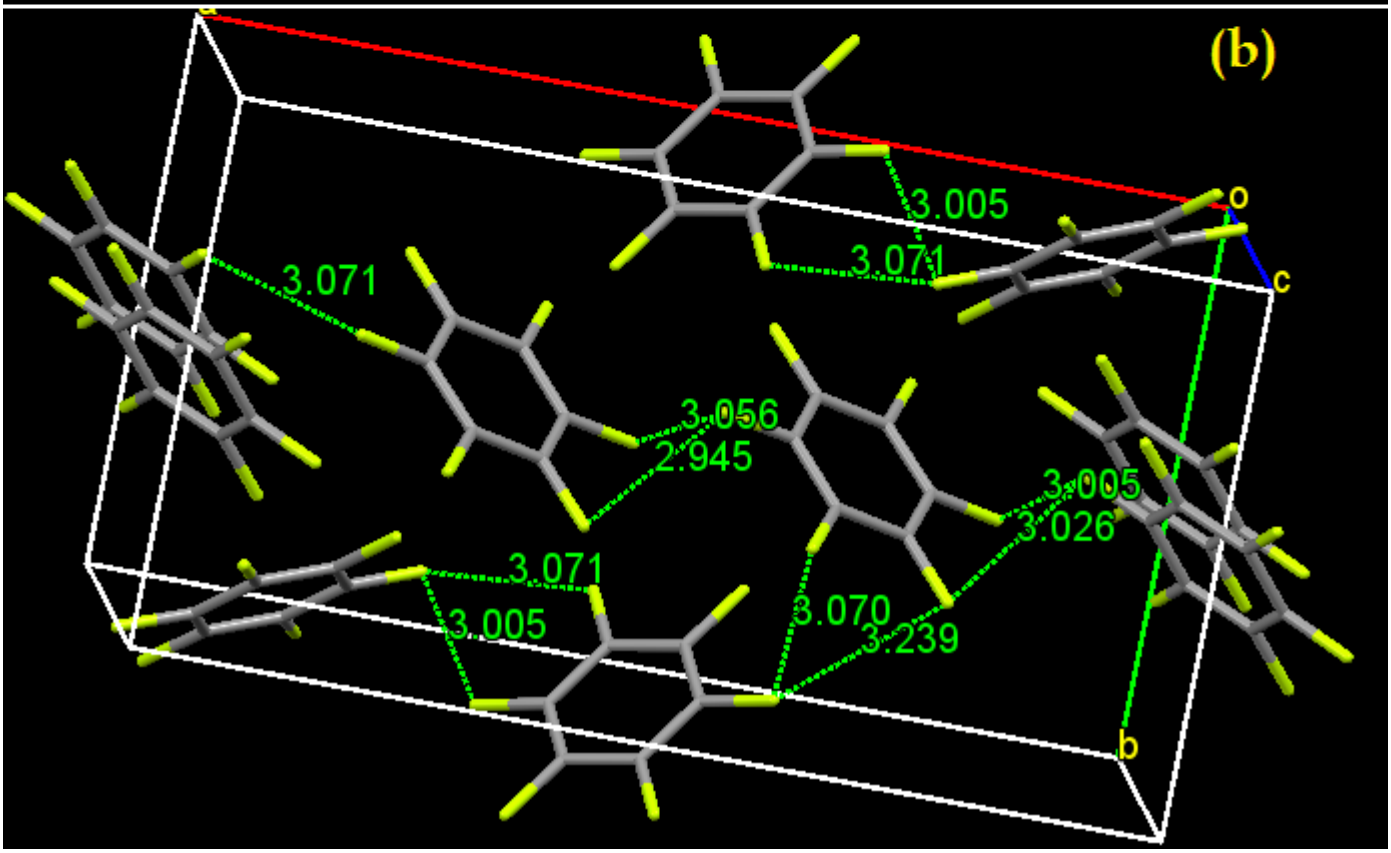


Fig. S1: RDG s vs. sign(λ_2)×ρ (in a.u.) plots for the three trimers of the C_6F_6 molecule, computed with M06-2X/6-311++G(d,p). The spikes in the sign(λ_2)×ρ < 0 and sign(λ_2)×ρ > 0 regions represent to the attractive and repulsive interactions, respectively. The s = 0.6 a.u. RDG isosurfaces in ball and stick models representing to the former and latter interactions are painted in green and red, respectively. For clarity, two different views are presented for (a). See Fig. 8 for geometric details, and Fig. 10a-c for QTAIM based molecular graphs.

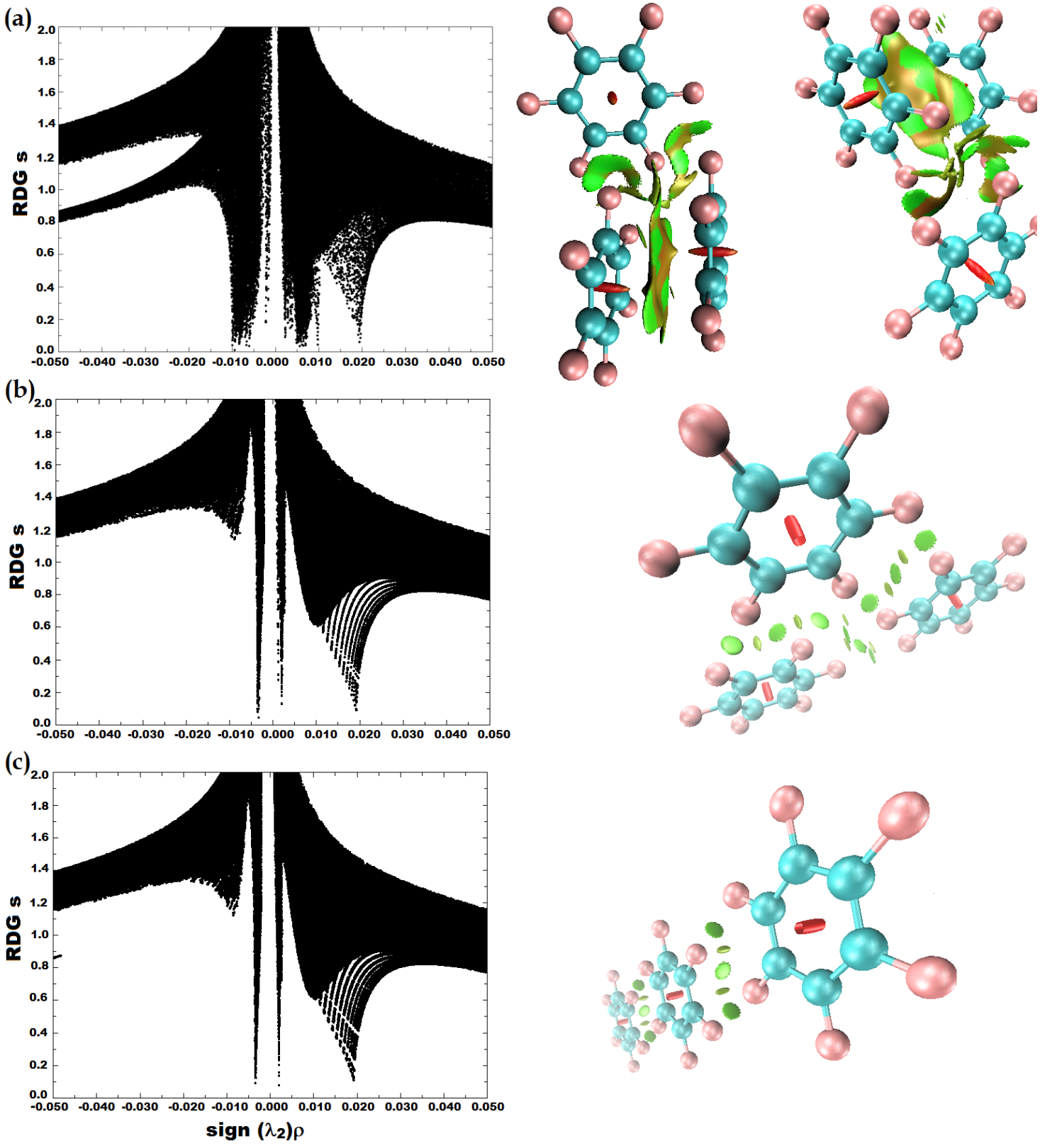


Table S1: Selected QTAIM based topological properties of the charge density of all the twelve $(C_6F_6)_2$ binary complexes examined, obtained with M06-2X/6-311++G(d,p).[a],[b]

Conformation	(3,–1) bcp	ρ_b	λ_1	λ_2	λ_3	$\nabla^2\rho_b$	V_b	G_b	H_b	DI
a[c]	F17 C11	0.0064	-0.0034	-0.0031	0.0306	0.0241	-0.0042	0.0051	0.0009	0.0210
	C4 C7	0.0089	-0.0046	-0.0031	0.0335	0.0257	-0.0045	0.0055	0.0010	0.0221
b	F22 F15	0.0071	-0.0036	-0.0026	0.0424	0.0362	-0.0068	0.0079	0.0011	0.0231
	C8 C2	0.0100	-0.0071	-0.0025	0.0399	0.0304	-0.0053	0.0065	0.0011	0.0238
	F17 F20	0.0019	-0.0015	-0.0007	0.0144	0.0121	-0.0015	0.0023	0.0008	0.0086
c[c]	F16 F22	0.0055	-0.0048	-0.0040	0.0367	0.0279	-0.0051	0.0061	0.0009	0.0217
	C3 C8	0.0108	-0.0074	-0.0038	0.0449	0.0337	-0.0062	0.0073	0.0011	0.0258
d	F8 F24	0.0069	-0.0068	-0.0034	0.0454	0.0351	-0.0067	0.0077	0.0010	0.0249
	F9 C21	0.0086	-0.0072	-0.0021	0.0473	0.0380	-0.0064	0.0080	0.0016	0.0191
	F9 F23	0.0084	-0.0074	-0.0036	0.0513	0.0402	-0.0082	0.0091	0.0009	0.0252
	F9 F24	0.0084	-0.0074	-0.0036	0.0513	0.0403	-0.0082	0.0091	0.0009	0.0252
	C3 F24	0.0078	-0.0058	-0.0020	0.0425	0.0346	-0.0058	0.0072	0.0014	0.0165
	C3 F23	0.0078	-0.0058	-0.0020	0.0425	0.0346	-0.0058	0.0072	0.0014	0.0165
	F10 F23	0.0069	-0.0068	-0.0034	0.0453	0.0351	-0.0067	0.0077	0.0010	0.0249
e[c]	F7 F17	0.0014	-0.0013	-0.0012	0.0119	0.0094	-0.0010	0.0017	0.0007	0.0070
	F8 F16	0.0100	-0.0096	-0.0024	0.0612	0.0492	-0.0100	0.0112	0.0011	0.0307
	F8 C13	0.0100	-0.0081	-0.0036	0.0556	0.0440	-0.0084	0.0097	0.0013	0.0298
f[c]	F18 C8	0.0060	-0.0040	-0.0002	0.0294	0.0251	-0.0042	0.0052	0.0010	0.0175
	F18 C9	0.0060	-0.0040	-0.0001	0.0294	0.0252	-0.0042	0.0052	0.0011	0.0171
g[c]	C12 F18	0.0059	-0.0039	-0.0003	0.0289	0.0246	-0.0041	0.0051	0.0010	0.0174
	C9 F18	0.0057	-0.0038	-0.0002	0.0279	0.0240	-0.0040	0.0050	0.0010	0.0167
h[c]	F17 F19	0.0036	-0.0035	-0.0034	0.0276	0.0207	-0.0032	0.0042	0.0010	0.0141
	F17 F20	0.0039	-0.0037	-0.0036	0.0302	0.0229	-0.0037	0.0047	0.0010	0.0173
i[c]	F19 F17	0.0050	-0.0050	-0.0048	0.0370	0.0050	-0.0048	0.0058	0.0010	0.0211
j	F16 F8	0.0053	-0.0048	-0.0048	0.0399	0.0303	-0.0053	0.0064	0.0011	0.0250
k	F8 F16	0.0052	-0.0047	-0.0047	0.0393	0.0299	-0.0052	0.0064	0.0011	0.0247
l	F8 F16	0.0045	-0.0041	-0.0039	0.0344	0.0264	-0.0045	0.0055	0.0010	0.0217

[a] See Fig. 1 for details of atom labeling and conformation type. See Fig. 4 for QTAIM based molecular graph.

[b] The properties include the charge density ρ_b, the three principal eigenvalues of the Hessian of the charge density matrix $\lambda_{i\ (i=1\text{-}3)}$, the Laplacian of the charge density $\nabla^2\rho_b$, the gradient kinetic energy density G_b, the potential energy density V_b, the total energy density H_b, and .1 a.u. of ρ_b = 6.7483 eÅ^{-3}; 1 a.u. of λ_i's or $\nabla^2\rho_b$ = 24.099 eÅ^{-5}; 1 a.u. of V_b, or G_b, or H_b = 627.504 kcal mol^{-1}.

[c] Values of selected bonds are shown for symmetry reasons.

Table S2: Selected QTAIM based topological properties of the charge density for the three trimers of the $(C_6F_6)_3$ complex, obtained with M06-2X/6-311++G(d,p).[a,b]

Conformation	(3,–1) bcp	ρ_b	λ_1	λ_2	λ_3	$\nabla^2\rho_b$	V_b	G_b	H_b	DI
a	F24 F11	0.0091	-0.0089	-0.0082	0.0581	0.0410	-0.0089	0.0096	0.0007	0.0315
	F23 F11	0.0079	-0.0078	-0.0074	0.0537	0.0385	-0.0077	0.0087	0.0010	0.0303
	F34 F11	0.0082	-0.0086	-0.0080	0.0557	0.0391	-0.0079	0.0088	0.0010	0.0315
	F24 F10	0.0078	-0.0077	-0.0067	0.0531	0.0387	-0.0077	0.0087	0.0010	0.0302
	F33 F12	0.0100	-0.0096	-0.0046	0.0627	0.0485	-0.0099	0.0110	0.0011	0.0347
	F34 F12	0.0053	-0.0052	-0.0050	0.0375	0.0274	-0.0049	0.0059	0.0010	0.0195
	C13 F34	0.0067	-0.0039	-0.0024	0.0318	0.0254	-0.0044	0.0054	0.0010	0.0203
	C17 C27	0.0094	-0.0052	-0.0021	0.0351	0.0278	-0.0047	0.0058	0.0011	0.0206
	C15 C25	0.0084	-0.0038	-0.0015	0.0294	0.0241	-0.0040	0.0050	0.0010	0.0184
	F33 C3	0.0099	-0.0078	-0.0032	0.0573	0.0463	-0.0083	0.0099	0.0017	0.0264
b	F9 F22	0.0035	-0.0033	-0.0032	0.0278	0.0212	-0.0033	0.0043	0.0010	0.0158
	F10 F35	0.0035	-0.0033	-0.0032	0.0277	0.0212	-0.0033	0.0043	0.0010	0.0147
	F10 F21	0.0035	-0.0033	-0.0032	0.0277	0.0212	-0.0033	0.0043	0.0010	0.0147
	F22 F10	0.0033	-0.0032	-0.0031	0.0258	0.0195	-0.0029	0.0039	0.0010	0.0132
	F11 F35	0.0033	-0.0032	-0.0031	0.0258	0.0195	-0.0029	0.0039	0.0010	0.0132
	F11 F34	0.0035	-0.0033	-0.0032	0.0278	0.0212	-0.0033	0.0043	0.0010	0.0158
	F21 F35	0.0035	-0.0033	-0.0032	0.0277	0.0212	-0.0033	0.0043	0.0010	0.0147
	F21 F36	0.0033	-0.0032	-0.0031	0.0258	0.0195	-0.0029	0.0039	0.0010	0.0132
	F19 F36	0.0035	-0.0033	-0.0032	0.0278	0.0212	-0.0033	0.0043	0.0010	0.0058
c	F9 F34	0.0035	-0.0033	-0.0031	0.0272	0.0208	-0.0032	0.0042	0.0010	0.0154
	F10 F33	0.0035	-0.0033	-0.0031	0.0272	0.0208	-0.0032	0.0042	0.0010	0.0154
	F10 F34	0.0034	-0.0033	-0.0032	0.0263	0.0198	-0.0030	0.0040	0.0010	0.0135
	F20 F7	0.0035	-0.0033	-0.0031	0.0272	0.0208	-0.0032	0.0042	0.0010	0.0154
	F21 F7	0.0034	-0.0033	-0.0032	0.0263	0.0198	-0.0030	0.0040	0.0010	0.0135
	F21 F12	0.0035	-0.0033	-0.0031	0.0272	0.0208	-0.0032	0.0042	0.0010	0.0154

[a] See Fig. 8 for details of atom labeling and conformation type. See Fig. 10 for QTAIM based molecular graph.

[b] The properties include the charge density ρ_b, the three principal eigenvalues of the Hessian of the charge density matrix $\lambda_{i\ (i=1\text{-}3)}$, the Laplacian of the charge density $\nabla^2\rho_b$, the gradient kinetic energy density G_b, the potential energy density V_b, the total energy density H_b, and .1 a.u. of ρ_b = 6.7483 eÅ^{-3}; 1 a.u. of λ_i's or $\nabla^2\rho_b$ = 24.099 eÅ^{-5}; 1 a.u. of V_b, or G_b, or H_b = 627.509 kcal mol^{-1}.

Table S3: Selected QTAIM based topological properties of the charge density for the two tetramers of the $(C_6F_6)_4$ complex, obtained with M06-2X/6-311++G(d,p).[a,b]

Conformation	(3,–1) bcp	ρ_b	λ_1	λ_2	λ_3	$\nabla^2\rho_b$	V_b	G_b	H_b	DI
a	F19 F36	0.0038	-0.0036	-0.0034	0.0292	0.0222	-0.0035	0.0046	0.0010	0.0167
	F21 F10	0.0036	-0.0034	-0.0033	0.0282	0.0215	-0.0034	0.0044	0.0010	0.0149
	F21 F35	0.0038	-0.0036	-0.0035	0.0298	0.0226	-0.0036	0.0046	0.0010	0.0160
	F21 F36	0.0034	-0.0033	-0.0032	0.0266	0.0200	-0.0030	0.0040	0.0010	0.0136
	F22 F10	0.0036	-0.0035	-0.0034	0.0277	0.0208	-0.0032	0.0042	0.0010	0.0143
	F22 F9	0.0037	-0.0035	-0.0034	0.0290	0.0221	-0.0035	0.0045	0.0010	0.0154
	F44 F22	0.0036	-0.0034	-0.0033	0.0281	0.0214	-0.0034	0.0044	0.0010	0.0149
	F23 F44	0.0031	-0.0030	-0.0030	0.0249	0.0189	-0.0028	0.0037	0.0010	0.0127
	F45 F23	0.0035	-0.0033	-0.0032	0.0276	0.0211	-0.0033	0.0043	0.0010	0.0157
	F10 F35	0.0034	-0.0032	-0.0031	0.0269	0.0206	-0.0032	0.0042	0.0010	0.0142
	F35 F11	0.0031	-0.0030	-0.0029	0.0245	0.0186	-0.0027	0.0037	0.0010	0.0125
	F11 F34	0.0033	-0.0031	-0.0030	0.0265	0.0203	-0.0031	0.0041	0.0010	0.0150
	F44 F9	0.0043	-0.0042	-0.0040	0.0330	0.0248	-0.0041	0.0052	0.0010	0.0179
	F43 F9	0.0037	-0.0036	-0.0035	0.0284	0.0213	-0.0033	0.0043	0.0010	0.0145
	F43 F8	0.0045	-0.0043	-0.0041	0.0338	0.0254	-0.0043	0.0053	0.0010	0.0196
b	F24 F48	0.0036	-0.0034	-0.0033	0.0283	0.0215	-0.0034	0.0044	0.0010	0.0161
	F24 F44	0.0034	-0.0033	-0.0032	0.0263	0.0199	-0.0030	0.0040	0.0010	0.0134
	F23 F44	0.0035	-0.0033	-0.0032	0.0274	0.0209	-0.0033	0.0042	0.0010	0.0155
	F7 F21	0.0027	-0.0026	-0.0025	0.0219	0.0168	-0.0023	0.0033	0.0009	0.0110
	F7 F20	0.0030	-0.0028	-0.0027	0.0242	0.0187	-0.0028	0.0037	0.0010	0.0137
	F12 F21	0.0030	-0.0028	-0.0027	0.0242	0.0187	-0.0028	0.0037	0.0010	0.0137
	F34 F9	0.0035	-0.0033	-0.0032	0.0274	0.0209	-0.0033	0.0042	0.0010	0.0155
	F33 F10	0.0036	-0.0034	-0.0033	0.0283	0.0215	-0.0034	0.0044	0.0010	0.0161
	F34 F10	0.0034	-0.0033	-0.0032	0.0263	0.0199	-0.0030	0.0040	0.0010	0.0134

[a] See Fig. 9 for details of atom labeling and conformation type. See Fig. 10 for QTAIM based molecular graph.

[b] The properties include the charge density ρ_b, the three principal eigenvalues of the Hessian of the charge density matrix $\lambda_{i\ (i=1-3)}$, the Laplacian of the charge density $\nabla^2\rho_b$, the gradient kinetic energy density G_b, the potential energy density V_b, the total energy density H_b, and .1 a.u. of ρ_b = 6.7483 eÅ^{-3}; 1 a.u. of λ_i's or $\nabla^2\rho_b$ = 24.099 eÅ^{-5}; 1 a.u. of V_b, or G_b, or H_b = 627.504 kcal mol^{-1}.

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