SUPPORTING INFORMATION

Structural Characterization of Dimeric Perfluoroalkyl Carboxylic Acid Using Experimental and Theoretical Ion Mobility Spectrometry Analyses

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Contents

1. Experimental section

1.1. LC conditions

Chromatographic separation was performed using a flow rate of 0.2 mL/min with a binary mobile phase gradient of solvent A (water + 0.1% formic acid) and solvent B (acetonitrile). The gradient was adapted from the literature[1] and started at 20% B and increased linearly from 20% to 40% (0-0.5 min); remained constant for 1 min (0.5-1.5 min); increased linearly from 40% to 100% for 10 min (1.5-11.5 min); remained constant at 100% until 19.5 min; and finally decreased from 100% to 20% (19.5-20 min).

1.2. Instrumental parameters

DTIM: ESI gas temperature and sheath gas temperature were 300°C and 350°C, respectively. Drying gas and sheath gas flow rates were set at 8 and 10 L/min, respectively, while nebulizer pressure was 35 psi. Applied voltages were 3500 V for the capillary, 1000 V for the nozzle and 320 V for the fragmentor. High-purity nitrogen was used as the drift gas in the drift tube cell, and the gas pressure in the cell was maintained at 3.95 Torr. The drift tube settings used are summarized in Table S1. They were based on the parameters used for the ^{DTIM}CCS database of the C_5-C_5 to C_{16}-C_{16} $[2M-H]^-$ dimers[2]. However, trap fill time, trap release time and trap funnel RF were adapted to increase the proportion of dimers to monomers. Single-field calibration was used for $^{DTIM}CCS_{N2}$ measurements, the reference CCS values used were from Stow et al[3]. In this approach, a set of reference ions with known *m/z* and $^{DTIM}CCS_{N2}$ are analyzed under the same conditions as the compounds of interest, enabling the calculation of $^{DTIM}CCS_{N2}$ values[2]. The ESI low-concentration tune mixture (Agilent Technologies, Santa Clara, USA) was used as the reference standard.

Table S1. Drift tube parameters used for the measurements of the CCSs of PFCA dimers.

Drift tube entrance voltage (V)	-1574
Drift tube exit voltage (V)	-224
Rear funnel entrance (V)	-217.5
Rear funnel exit (V)	-45
Trap funnel RF (V)	-120
High pressure Funnel RF (V)	-120
Acquisition mode	Single pulse IM-QTOF
Trap fill time (µs)	15000
Trap release time (µs)	250
Max. drift time (ms)	60
IM transient rate (transients/frame)	17
Frame rate (frame/sec)	0.9

TIMS: The electrospray source was operated in negative mode with a dry temperature of 180°C and a nebulizer pressure of 0.5 bar. The end plate offset and capillary voltages were set at 500 V and 2000 V, respectively and the dry gas flow rate applied was 4 L/min. The mass range analyzed was 50 to 2000 *m/z* and the inverse reduced ion mobility range scanned was from $1/K_0 = 0.4$ to 1.93. Ions were accumulated for 300 ms before being separated in the TIMS cell with a ramp time of 300 ms, leading to a 100% duty cycle. High-purity nitrogen was used as the buffer gas in the TIMS cell and the pressure at the TIMS cell entrance was 2.74 mbar and 0.89 mbar at the mobility cell exit. The TIMS parameters used for PFCA dimer analysis are summarized in Table S2. They were chosen to favor the detection of as many dimeric PFCA ions as possible within the mobility range scanned. In TIMS, the relation between the elution voltage and inverse reduced ion mobility ($1/K_0$) is virtually linear. Therefore, ion mobility values were calibrated using the ESI low-concentration tune mixture (Agilent Technologies, Santa Clara, USA) as a reference standard, using the same TIMS parameters as for the compounds of interest. Measured mobility values were converted into CCS values during data processing. The reference ions used were *m/z* 301.9981 ($1/K_0 = 0.6678$), *m/z* 601.979 ($1/K_0 = 0.8782$), *m/z* 1033.9881 ($1/K_0 = 1.2526$), *m/z* 1333.9689 ($1/K_0 = 1.4016$), *m/z* 1633.9498 ($1/K_0 = 1.5731$), and *m/z* 1933.9306 ($1/K_0 = 1.7452$.).

Table S2. TIMS parameters used for the measurements of the CCSs of PFCA dimers.

General		**TIMS**	
Deflection delta (V)	-70	Δ1 (V)	-20
isCID energy (eV)	0	Δ2 (V)	-120
Funnel 1 RF (Vpp)	500	Δ3 (V)	-50
Funnel 2 RF (Vpp)	250	Δ4 (V)	-250

Multipole RF (Vpp)	250	Δ5 (V)	-150
Ion Energy (eV)	8	Δ6 (V)	-150
Low mass (m/z)	50	Funnel 1 RF (Vpp)	250
Collision Energy (eV)	8	Collision cell in (V)	-200
Transfer Time (µs)	70		
Collision RF (Vpp)	1000		
Pre-pulse storage (µs)	5		

TWIMS: The source and desolvation temperatures of the ESI source, operated in negative mode, were 150 and 200°C, respectively. Cone and desolvation gas flow rates were 5 and 650 L/h, respectively. The applied voltages were 2000 V (ESI), 12 V (sampling cone), 1.5 V (extraction voltage). The wave velocity and the wave height in the ion mobility cell were 300 m/s and 27 V, respectively, and the selected mass range was 50 to 5000 *m/z*. The selected gas flow parameters were 4 mL/min (source transfer), 4 mL/min (trap), 90 mL/min (helium cell), 180 mL/min (IMS cell, with a N_2 pressure of 3.81mbar). The ESI low-concentration tune mixture (Agilent Technologies, Santa Clara, USA) was also acquired at the start of each analysis day, with the same conditions as for PFCAs, to convert the measured arrival times of the compounds of interest into CCS values. The reference ions used were *m/z* 601.979 (CCS = 139.8 Å^2), *m/z* 1033.9881 (CCS = 179.9 Å^2), *m/z* 1333.9689 (CCS = 254.2 Å^2), *m/z* 1633.9498 (CCS = 283.6 Å^2), *m/z* 1933.9306 (CCS = 317.7 Å^2), *m/z* 2233.9115 (CCS = 352 Å^2), and 2533.8923 (CCS = 380 Å^2).

1.3. Data processing

DTIM: DTIM data were first recalibrated against the reference mass solution using the IM-MS Data File Reprocessing Utility (version 10.00, Agilent Technologies) to ensure high mass accuracy. The Agilent IM-MS Browser (version 10.00) was used and the signals of most of the compounds of interest were searched for and extracted based on the feature extraction algorithm. Subsequently, $^{DTIM}CCS_{N2}$ values were calculated by applying the single-field calibration algorithm. The reported values were the averaged $^{DTIM}CCS_{N2}$ value obtained from five injections, and the standard and relative standard deviations were calculated.

TIMS: TIMS data were processed with DataAnalysis v4.0. First, the mobilograms of the ions of interest were extracted based on their *m/z* ratio. The mobility peaks of interest were then integrated, and the mobility values (K_0) were converted into $^{TIMS}CCS_{N2}$ values by the software, based on the Mason-Schamp equation. As with DTIM, the reported values were the averaged $^{TIMS}CCS_{N2}$ value obtained from five injections, and the standard and relative standard deviations were calculated.

TWIMS: TWIMS data were first processed with MassLynx (version 4.1). The arrival time distributions of the ions interest were extracted on the basis of their *m/z* ratio and smoothed using a Savistky-Golay algorithm (window size = ± 2 scans, number of smooth = 3). The smoothed data were exported, and they were fitted using a gaussian fitting model with Igor Pro v.6.3.2 (WaveMetrics, Inc., Portland, USA). The center values of the Gaussian fitting curves were then reported for each ion and converted to $^{TWIMS}CCS_{N2}$ values, based on the calibration performed with the Agilent tune mix. In TWIMS, the relation between arrival time and the derived CCS value is a power law[4]. Consequently, the power regression model between the arrival times and known CCS values of the Agilent tune mix was calculated and the same function was used to derive CCS values from the arrival times of the PFCA ions. Ideally, for calibration in TWIMS, the calibration ions should match the chemical class and ion charge state of the analytes[5]. The Agilent tune mix consists of compounds including a fluorinated part and presenting a single negative charge when ionized. So, it can be used for the CCS calibration of the PFAS in a first approximation. Seven ions of the ATM mixture were detected, leading to a calibration in the CCS range between 139.8 and 380 Å^2. The reported values for PFCAs were the average $^{TWIMS}CCS_{N2}$ value obtained from three injections, and the standard and relative standard deviations were calculated.

1.4. Experimental CCS values

Table S3. Measured $^{DTIM}CCS_{N2}$, $^{TIMS}CCS_{N2}$ and $^{TWIMS}CCS_{N2}$ values for monomeric $[M-H]^-$ PFCA ions.

Acronym	*m/z* ($[M-H]^-$)	Observed mean $^{DTIM}CCS_{N2}$ value ($Å^2$)	2SD (DTIM)	Observed mean $^{TIMS}CCS_{N2}$ value ($Å^2$)	2SD (TIMS)	% Dif. TIMS vs DTIM CCS	Observed mean $^{TWIMS}CCS_{N2}$ value ($Å^2$)	2SD (TWIMS)	% Dif. TWIMS vs DTIM CCS
PFHxA	312.9728	**139.13**	0.39						
PFHpA	362.9696	**147.56**	0.10						
PFOA	412.9664	**156.72**	0.27				**153.59**	0.18	-2.0
PFNA	462.9632	**165.73**	0.06	**162.62**	0.53	-1.9	**163.40**	0.12	-1.4
PFDA	512.96	**174.74**	0.09	**171.25**	0.06	-2.0	**172.85**	0.22	-1.1
PFUnDA	562.9568	**183.45**	0.08	**181.06**	0.27	-1.3			
PFDoDA	612.9536	**192.39**	0.04	**190.08**	0.03	-1.2			
PFTrDA	662.9505	**201.52**	0.05	**199.78**	0.20	-0.9			
PFTeDA	712.9473	**210.16**	0.16	**207.42**	0.21	-1.3	**208.09**	0.20	-1.0
PFHxDA	812.9409	**227.96**	0.10	**225.39**	0.70	-1.1			
PFODA	912.9345	**244.08**	0.06	**242.14**	0.32	-0.8	**242.37**	0.22	-0.7

Table S4. Measured $^{DTIM}CCS_{N2}$, $^{TIMS}CCS_{N2}$ and $^{TWIMS}CCS_{N2}$ values for homodimeric $[2M-H]^-$ PFCA ions.

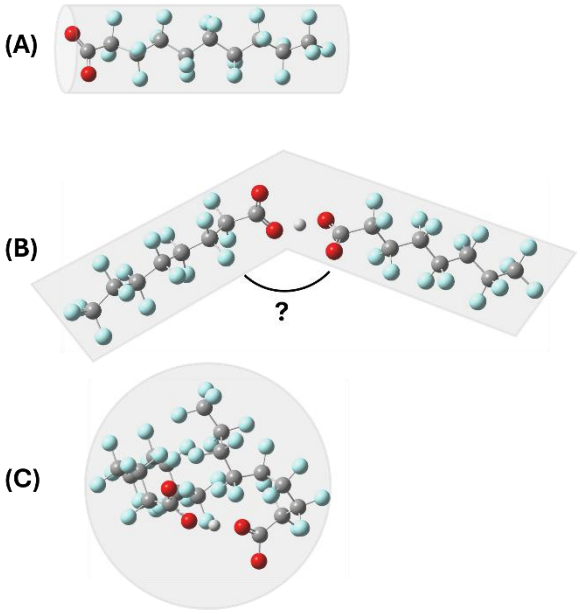
Acronym	*m/z* ($[2M-H]^-$)	Observed mean $^{DTIM}CCS_{N2}$ value ($Å^2$)	2SD (DTIM)	Observed mean $^{TIMS}CCS_{N2}$ value ($Å^2$)	2SD (TIMS)	% Dif. TIMS vs DTIM CCS	Observed mean $^{TWIMS}CCS_{N2}$ value ($Å^2$)	2SD (TWIMS)	% Dif. TWIMS vs DTIM CCS
PFBA	426.9657	**162.77**	0.47						
PFPeA	526.9593	**179.86**	0.48						
PFHxA	626.9529	**196.34**	0.87	**194.57**	0.23	-0.9			
PFHpA	726.9465	**211.57**	0.19	**209.93**	0.06	-0.8			
PFOA	826.9401	**226.59**	0.24	**225.63**	0.14	-0.4	**226.83**	0.26	0.1
PFNA	926.9337	**240.74**	0.11	**240.13**	0.19	-0.3	**241.47**	0.18	0.3
PFDA	1026.9273	**254.82**	0.14	**253.65**	0.07	-0.5	**255.13**	0.13	0.1
PFUnDA	1126.9210	**267.28**	0.18	**267.70**	0.02	0.2			
PFDoDA	1226.9146	**279.01**	0.38	**280.36**	0.05	0.5			
PFTrDA	1326.9082	**290.95**	0.31	**292.55**	0.27	0.5			
PFTeDA	1426.9018	**302.26**	0.96	**304.32**	0.08	0.7	**303.96**	0.08	0.6
PFHxDA	1626.8890	**325.67**	0.40	**327.06**	0.09	0.4			
PFODA	1826.8762	**348.47**	0.29	**349.62**	0.17	0.3	**350.05**	0.37	0.5

Table S5. Measured $^{DTIM}CCS_{N2}$, $^{TIMS}CCS_{N2}$ and $^{TWIMS}CCS_{N2}$ values for $[2M-H]^-$ asymmetric isobaric PFCA ions (18 C atoms in total (m/z = 926.9337)).

# Fluorinated carbon atoms in each chain	Observed mean $^{DTIM}CCS_{N2}$ value (Å^2)	2SD (DTIM)	Observed mean $^{TIMS}CCS_{N2}$ value (Å^2)	2SD (TIMS)	% Dif. TIMS vs DTIM CCS	Observed mean $^{TWIMS}CCS_{N2}$ value (Å^2)	2SD (TWIMS)	% Dif. TWIMS vs DTIM CCS
1-15	**246.93**	0.40	**245.05**	0.40	-0.8			
3-13	**244.26**	0.43	**243.23**	0.14	-0.4	**243.87**	0.80	0.2
4-12	**243.43**	0.22	**242.49**	0.19	-0.4			
5-11	**242.21**	0.11	**241.62**	0.11	-0.2			
6-10	**241.53**	0.15	**240.64**	0.03	-0.4			
7-9	**241.25**	0.17	**240.42**	0.13	-0.3	**241.49**	0.22	-0.1
8-8	**240.74**	0.11	**240.13**	0.19	-0.3	**241.48**	0.18	-0.3

2. Initial structural hypotheses

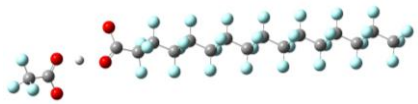
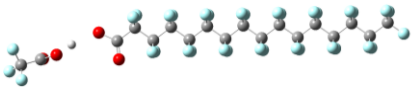
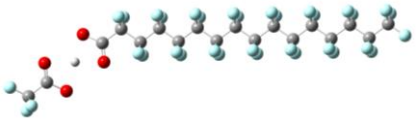
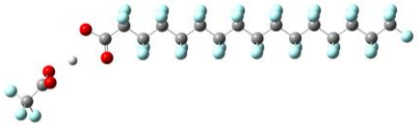
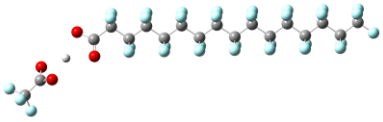
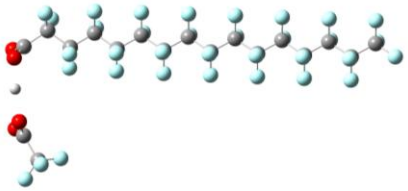
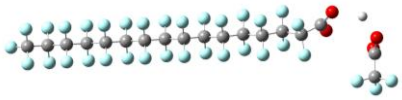
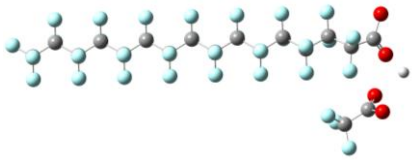
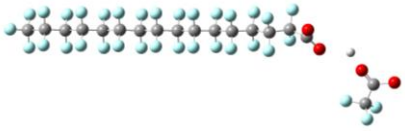
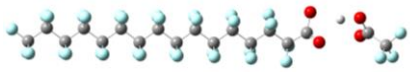
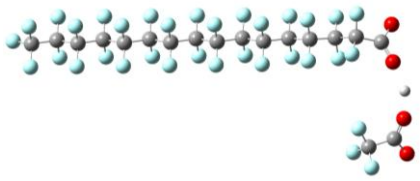
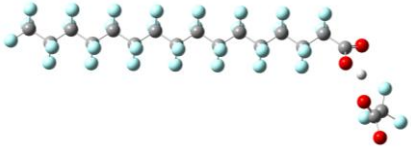
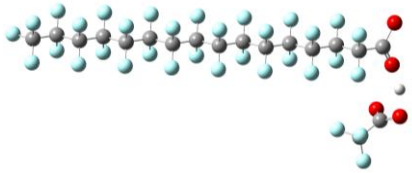
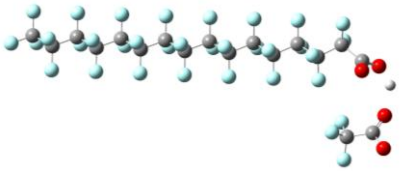
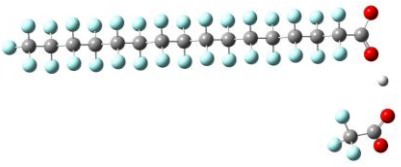
Figure S1. Schematic representation of the structures discussed with the CCS versus *m/z* trendlines. (A) Cylindrical structure of monomeric ions, (B) V-shaped structure of dimeric ions, (C) spherical structure of dimeric ions.



3. Quantum chemistry section

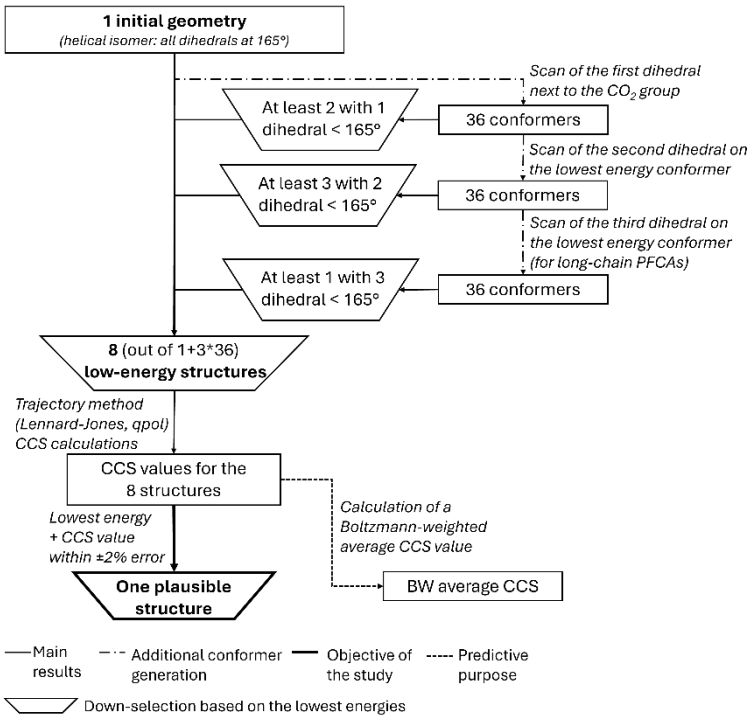
3.1. Initial dimer geometries

Figure S2. 15 Initial PFCA dimer geometries shown for the C_2-C_{16} dimer, before PM6 preoptimization.

#1  O_2C-H-CO_2 angle = 171.38°	**#2**  O_2C-H-CO_2 angle = 157.43°	**#3**  O_2C-H-CO_2 angle = 175.42°
#4  O_2C-H-CO_2 angle = 175.21°	**#5**  O_2C-H-CO_2 angle = 173.90°	**#6**  O_2C-H-CO_2 angle = 131.25°
#7  O_2C-H-CO_2 angle = 86.63°	**#8**  O_2C-H-CO_2 angle = 97.44°	**#9**  O_2C-H-CO_2 angle = 145.14°
#10  O_2C-H-CO_2 angle = 132.00°	**#11**  O_2C-H-CO_2 angle = 140.79°	**#12**  O_2C-H-CO_2 angle = 125.29°
#13  O_2C-H-CO_2 angle = 129.98°	**#14**  O_2C-H-CO_2 angle = 112.81°	**#15**  O_2C-H-CO_2 angle = 144.64°

3.2. Workflow for conformer generation of PFCA monomeric ions

Figure S3. Workflow for conformer generation and CCS calculations for PFCA monomeric ions. The dashed line indicates the selection of low-energy structures.



3.3. Results for PFCA monomeric ions

Table S6. Percentage difference between the predicted and DTIM experimental CCS values of monomeric PFCA ions.

	m/z (M-H)	M06-2X 6-31+G(d,p) **Mulliken**	M06-2X 6-31+G(d,p) **NBO**	M06-2X 6-311+G(d,p) **Mulliken**	CAM-B3LYP 6-31+G(d,p) **Mulliken**	WB97XD 6-31+G(d,p) **Mulliken**
C6	312.9728	-3.3	-2.60	-3.26	-0.37	-0.74
C7	362.9696	-3.6	-3.52			
C8	412.9664	-1.7	-1.66			
C9	462.9632	-2.1	-2.05	-1.39	1.24	1.14
C10	512.96	0.4	0.36			
C11	562.9568	0.6	0.88			
C12	612.9536	1.0	1.43	2.25	2.94	2.71
C13	662.9505	0.7	1.16			
C14	712.9473	0.4	1.09			
C16	812.9409	1.7	2.62	2.13	3.77	3.65
C18	912.9345	2.4	3.73			

Figure S4. Comparison of predicted (theoretical) and experimental CCS values for the monomeric PFCA ions. (A) Values obtained at the M06-2X/6-31+G(d,p) level of theory with Mulliken or NBO charge descriptors. (B) Values obtained with Mulliken charge descriptors, with different functionals and basis sets.

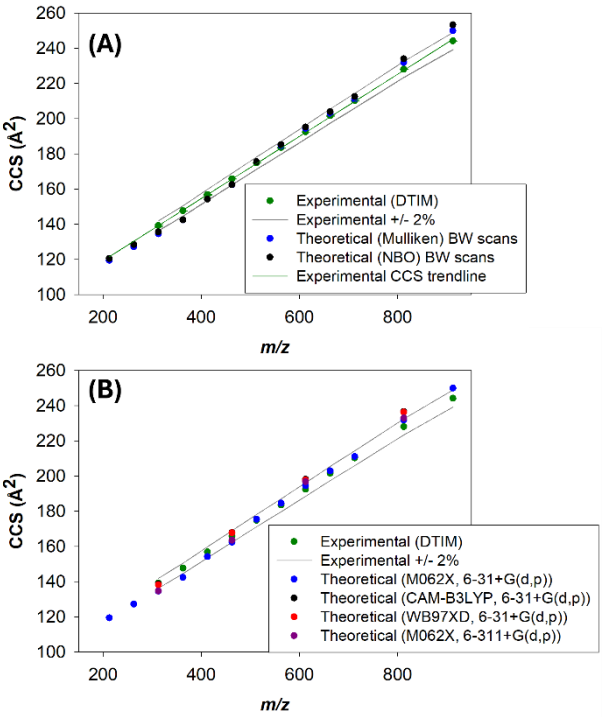
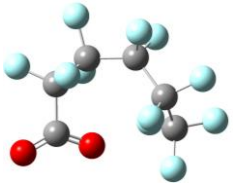


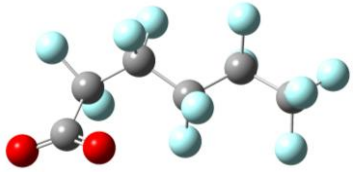
Figure S5. Structures of the eight C_6 PFCA conformers studied at the M06-2X/6-31+G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the O_2C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

#1
30% BW (+0.0 kcal/mol)



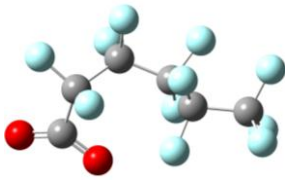
-5.63% (mulli) CO_2-CF_3 = 3.87 Å
-5.20% (NBO) Dip = 27.67 D

#2
30% BW (+0.0 kcal/mol)



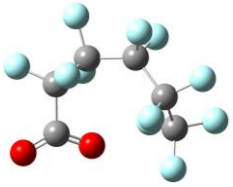
-1.71% (mulli) CO_2-CF_3 = 5.78 Å
-0.57% (NBO) Dip = 11.99 D

#3
8% BW (+0.8 kcal/mol)



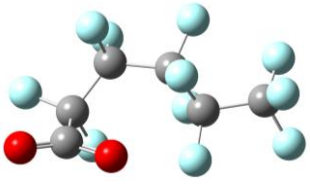
-1.54% (mulli) CO_2-CF_3 = 5.39 Å
-1.29% (NBO) Dip = 10.82 D

#4
8% BW (+0.8 kcal/mol)



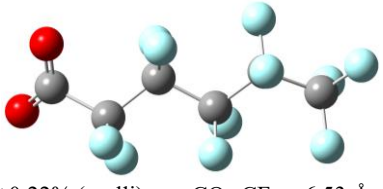
-6.03% (mulli) CO_2-CF_3 = 3.75 Å
-5.15% (NBO) Dip = 7.80 D

#5
8% BW (+0.8 kcal/mol)



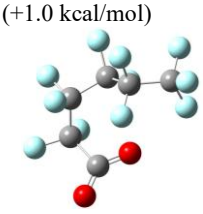
-2.28% (mulli) CO_2-CF_3 = 5.39 Å
-2.28% (NBO) Dip = 10.88 D

#6
7% BW (+0.9 kcal/mol)



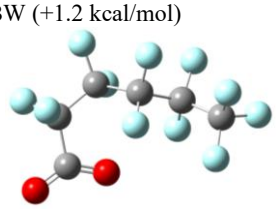
+0.22% (mulli) CO_2-CF_3 = 6.53 Å
+1.74% (NBO) Dip = 14.53 D

#7
6% BW (+1.0 kcal/mol)



-4.27% (mulli) CO_2-CF_3 = 4.32 Å
-3.58% (NBO) Dip = 8.27 D

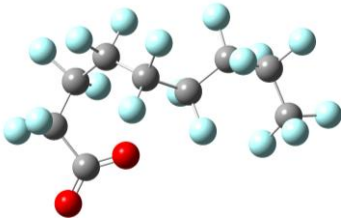
#8
4% BW (+1.2 kcal/mol)



-3.70% (mulli) CO_2-CF_3 = 4.97 Å
-2.93% (NBO) Dip = 9.93 D

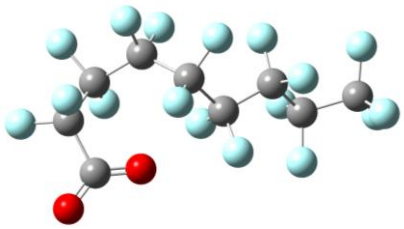
Figure S6. Structures of the eight C_9 PFCA conformers studied at the M06-2X/6-31+G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the O_2C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

#1
36% BW (+0.0 kcal/mol)



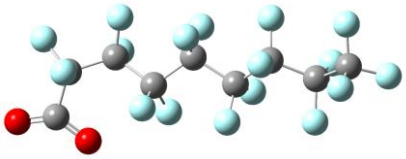
-4.01% (mulli) CO_2-CF_3 = 6.26 Å
-3.80% (NBO) Dip = 11.50 D

#2
27% BW (+0.2 kcal/mol)



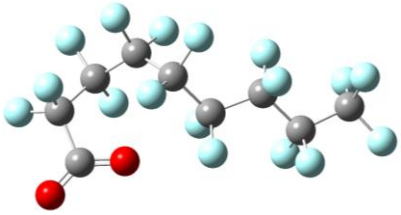
-2.28% (mulli) CO_2-CF_3 = 7.68 Å
-2.67% (NBO) Dip = 13.01 D

#3
15% BW (+0.5 kcal/mol)



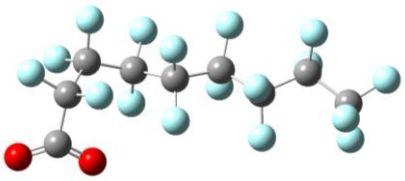
+1.52% (mulli) CO_2-CF_3 = 9.73 Å
+1.51% (NBO) Dip = 20.17 D

#4
8% BW (+0.9 kcal/mol)



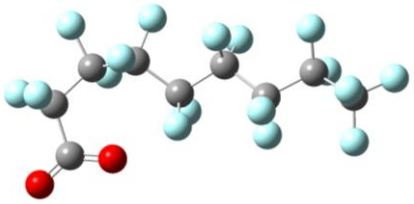
-2.89% (mulli) CO_2-CF_3 = 7.69 Å
-2.65% (NBO) Dip = 26.41 D

#5
5% BW (+1.2 kcal/mol)



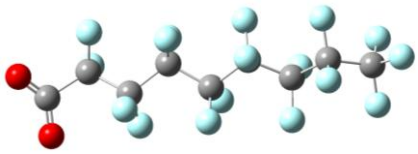
-0.41% (mulli) CO_2-CF_3 = 8.69 Å
-0.47% (NBO) Dip = 17.47 D

#6
3% BW (+1.5 kcal/mol)



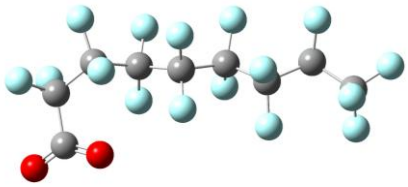
-0.68% (mulli) CO_2-CF_3 = 8.58 Å
-0.75% (NBO) Dip = 16.04 D

#7
3% BW (+1.5 kcal/mol)



+1.41% (mulli) CO_2-CF_3 = 10.38 Å
+2.87% (NBO) Dip = 23.08 D

#8
2% BW (+1.9 kcal/mol)



+0.21% (mulli) CO_2-CF_3 = 8.79 Å
+0.65% (NBO) Dip = 17.87 D

Figure S7. Structures of the eight C_{12} PFCA conformers studied at the M06-2X/6-31+G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the O_2C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

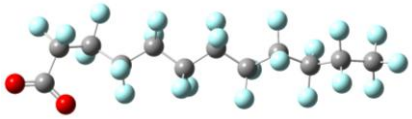
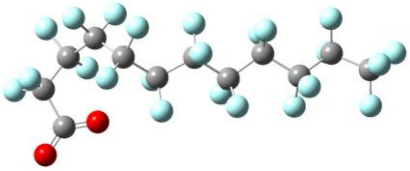
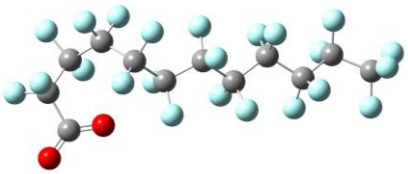
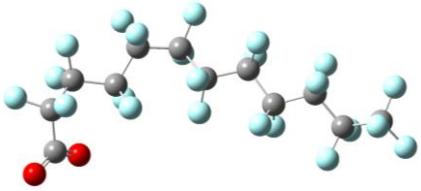
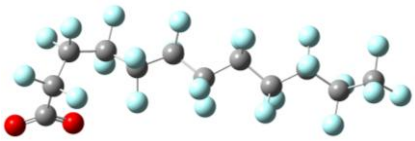
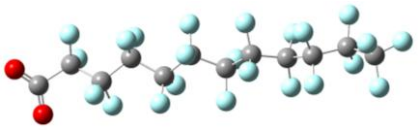
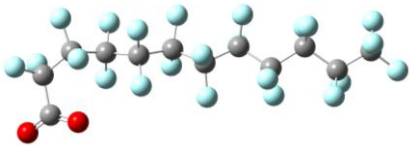
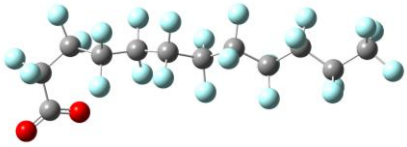
#1 27% BW (+0.0 kcal/mol)  +2.81% (mulli) CO_2-CF_3 = 13.56 Å +2.90% (NBO) Dip = 28.76 D	**#2** 18% BW (+0.3 kcal/mol)  -0.97% (mulli) CO_2-CF_3 = 11.29 Å -1.67% (NBO) Dip = 20.15 D	**#3** 18% BW (+0.3 kcal/mol)  -0.82% (mulli) CO_2-CF_3 = 11.29 Å -0.81% (NBO) Dip = 25.81 D
#4 17% BW (+0.3 kcal/mol)  +1.42% (mulli) CO_2-CF_3 = 11.65 Å +3.00% (NBO) Dip = 23.88 D	**#5** 11% BW (+0.6 kcal/mol)  +1.08% (mulli) CO_2-CF_3 = 12.61 Å +1.64% (NBO) Dip = 25.63 D	**#6** 5% BW (+1.0 kcal/mol)  +2.67% (mulli) CO_2-CF_3 = 14.22 Å +4.83% (NBO) Dip = 31.95 D
#7 3% BW (+1.3 kcal/mol)  +1.69% (mulli) CO_2-CF_3 = 12.73 Å +2.24% (NBO) Dip = 16.12 D	**#8** 3% BW (+1.3 kcal/mol)  +1.12% (mulli) CO_2-CF_3 = 12.72 Å +2.38% (NBO) Dip = 26.10 D	

Figure S8. Structures of the eight C_{16} PFCA conformers studied at the M06-2X/6-31+G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the O_2C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

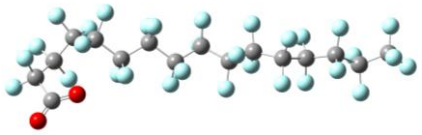
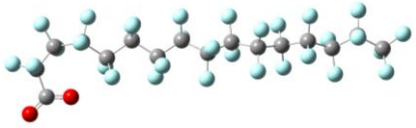
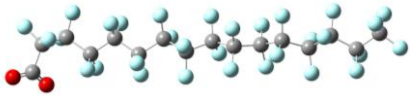
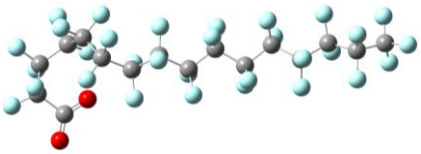
#1 47% BW (+0.0 kcal/mol)  +0.95% (mulli) CO_2-CF_3 = 16.41 Å +1.26% (NBO) Dip = 25.46 D	**#2** 16% BW (+0.7 kcal/mol)  +2.05% (mulli) CO_2-CF_3 = 17.43 Å +3.28% (NBO) Dip = 35.49 D	**#3** 12% BW (+0.8 kcal/mol)  +2.99% (mulli) CO_2-CF_3 = 17.76 Å +4.40% (NBO) Dip = 37.70 D
#4 8% BW (+1.0 kcal/mol)  +2.45% (mulli) CO_2-CF_3 = 18.54 Å +4.58% (NBO) Dip = 40.25 D	**#5** 7% BW (+1.1 kcal/mol)  +2.67% (mulli) CO_2-CF_3 = 17.73 Å +4.64% (NBO) Dip = 37.54 D	**#6** 4% BW (+1.5 kcal/mol)  -1.54% (mulli) CO_2-CF_3 = 15.05 Å -0.41% (NBO) Dip = 26.40 D
#7 4% BW (+1.4 kcal/mol)  +3.52% (mulli) CO_2-CF_3 = 18.66 Å +4.77% (NBO) Dip = 40.66 D	**#8** 1% BW (+2.5 kcal/mol)  +4.39% (mulli) CO_2-CF_3 = 19.41 Å +6.45% (NBO) Dip = 44.11 D	

Figure S9. Structures of the lowest-energy conformer for each monomeric PFCA ion, with a calculated CCS within 2% of DTIM experimental values, obtained at the M06-2X/6-31+G(d,p) level of theory. The Boltzmann weight and the energy difference relative to the global lowest-energy conformer are indicated. CCS deviations from DTIM experimental values are shown for both Mulliken (Mulli) and Natural Bond Order (NBO) partial charge descriptions. Additionally, the $O_2C–CF_3$ bond distance and the dipole moment are provided for each conformer.

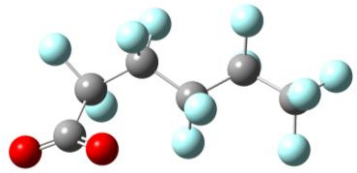
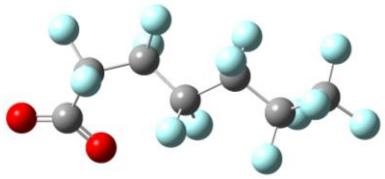
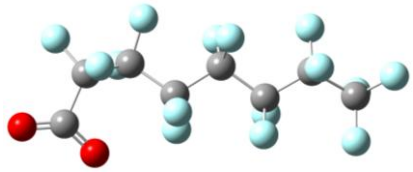
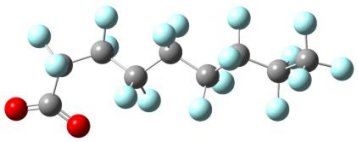
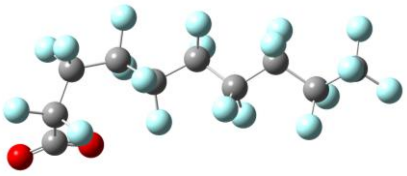
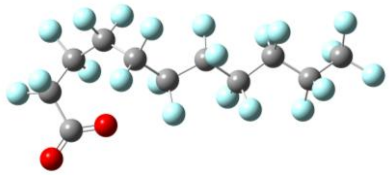
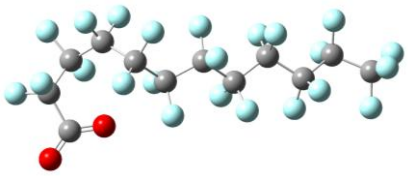
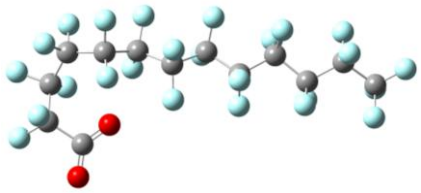
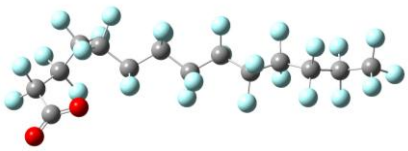
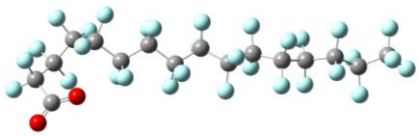
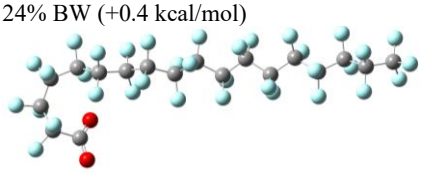
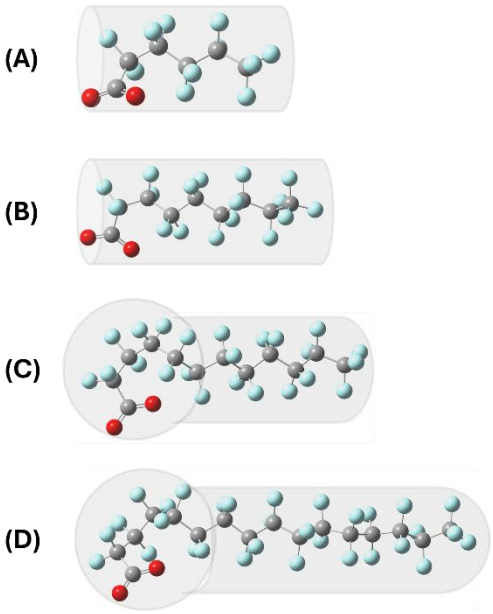
C_6 (#FC = 5) 30% BW (+0.0 kcal/mol)  -1.71% (mulli) CO_2-CF_3 = 5.78 Å -0.57% (NBO) Dip = 11.99 D	**C_7 (#FC = 6)** 11% BW (+0.7 kcal/mol)  +0.64% (mulli) CO_2-CF_3 = 7.22 Å +1.20% (NBO) Dip = 14.77 D	**C_8 (#FC = 7)** 20% BW (+0.5 kcal/mol)  +1.31% (mulli) CO_2-CF_3 = 8.41 Å +1.45% (NBO) Dip = 17.37 D
C_9 (#FC = 8) 15% BW (+0.5 kcal/mol)  +1.52% (mulli) CO_2-CF_3 = 9.73 Å +1.51% (NBO) Dip = 20.17 D	**C_{10} (#FC = 9)** 13% BW (+0.6 kcal/mol)  +0.36% (mulli) CO_2-CF_3 = 10.15 Å -0.18% (NBO) Dip = 20.25 D	**C_{11} (#FC = 10)** 12% BW (+0.3 kcal/mol)  -1.39% (mulli) CO_2-CF_3 = 10.08 Å -1.68% (NBO) Dip = 25.97 D
C_{12} (#FC = 11) 17% BW (+0.3 kcal/mol)  -0.82% (mulli) CO_2-CF_3 = 11.29 Å -0.80% (NBO) Dip = 25.81 D	**C_{13} (#FC = 12)** 31% BW (+0.0 kcal/mol)  -1.68% (mulli) CO_2-CF_3 = 11.24 Å -0. 30% (NBO) Dip = 19.69 D	**C_{14} (#FC = 13)** 46% BW (+0.0 kcal/mol)  +0.02% (mulli) CO_2-CF_3 = 13.85 Å -0.15% (NBO) Dip = 25.57 D
C_{16} (#FC = 15) 47% BW (+0.0 kcal/mol)  +0.95% (mulli) CO_2-CF_3 = 16.41 Å +1.26% (NBO) Dip = 25.46 D	**C_{18} (#FC = 17)** 24% BW (+0.4 kcal/mol)  +1.25% (mulli) CO_2-CF_3 = 17.06 Å +2.81% (NBO) Dip = 31.48 D	

Figure S10. Schematic representation of the overall shapes discussed for the monomeric ions with cylindrical (A, B) or "ball-cylinder" shapes (C,D).



3.4. Results for PFCA homodimeric ions

Figure S11. Optimized structures of the initial geometries for the C_9-C_9 PFCA dimer at the M06-2X/6-31+G(d,p) level of theory. Out of the 15 initial geometries, two were excluded as they had imaginary frequencies and are not shown. The Boltzmann weight is given, along with the energy difference with the least energetic geometry. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. The bolded box highlights the geometry with less than 2% error with Mulliken descriptors.

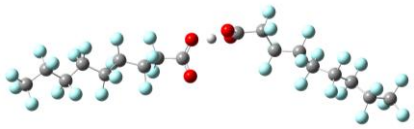
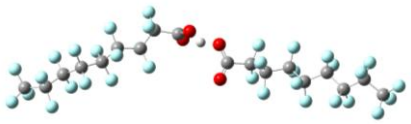
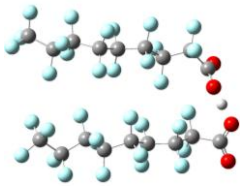
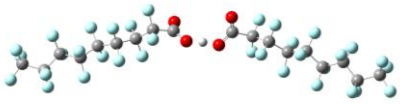
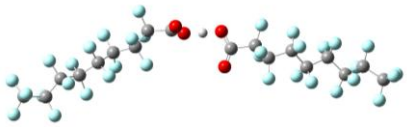
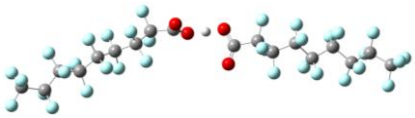
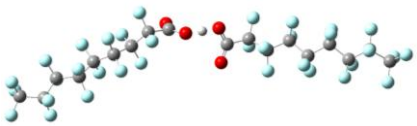
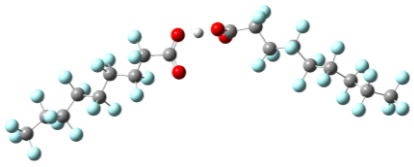
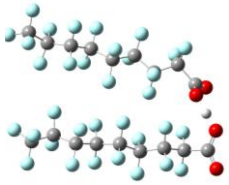
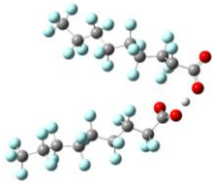
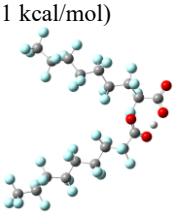
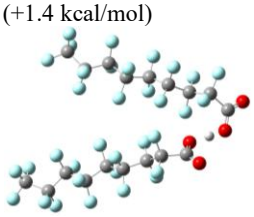
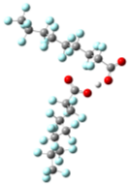
#1 15% BW (+0.0 kcal/mol)  +12.3% (mulli) CF_3-CF_3 = 22.65 Å +11.0% (NBO) Dip = 5.24 D	**#2** 14% BW (+0.0 kcal/mol)  +12.6% (mulli) CF_3-CF_3 = 22.79 Å +12.3% (NBO) Dip = 5.78 D	**#3** 14% BW (+0.0 kcal/mol)  -1.60% (mulli) CF_3-CF_3 = 5.65 Å -3.67% (NBO) Dip = 43.77 D
#4 12% BW (+0.1 kcal/mol)  +12.5% (mulli) CF_3-CF_3 = 23.92 Å +11.8% (NBO) Dip = 12.42 D	**#5** 9% BW (+0.3 kcal/mol)  +13.4% (mulli) CF_3-CF_3 = 23.28 Å +13.1% (NBO) Dip = 10.97 D	**#6** 9% BW (+0.3 kcal/mol)  +12.5% (mulli) CF_3-CF_3 = 23.69 Å +12.1% (NBO) Dip = 21.21 D
#7 9% BW (+0.3 kcal/mol)  +11.8% (mulli) CF_3-CF_3 = 23.52 Å +11.6% (NBO) Dip = 9.52 D	**#8** 7% BW (+0.5 kcal/mol)  +12.3% (mulli) CF3-CF_3 = 22.02 Å +12.2% (NBO) Dip = 6.27 D	**#9** 4% BW (+0.9 kcal/mol)  -2.82% (mulli) CF3-CF_3 = 6.39 Å -3.91% (NBO) Dip = 10.40 D
#10 2% BW (+1.1 kcal/mol)  +4.28% (mulli) CF_3-CF_3 = 11.49 Å +3.70% (NBO) Dip = 11.16 D	**#11** 2% BW (+1.1 kcal/mol)  +3.94% (mulli) CF_3-CF_3 = 11.49 Å +3.43% (NBO) Dip = 30.34 D	**#12** 2% BW (+1.4 kcal/mol)  +2.97% (mulli) CF_3-CF_3 = 8.27 Å +0.34% (NBO) Dip = 33.61 D
#13 <1% BW (+4.4 kcal/mol)  +8.41% (mulli) CF_3-CF_3 = 17.90 Å +7.93% (NBO) Dip = 25.18 D		

Figure S12. Effect of accounting for the parallel geometries for calculating the theoretical Boltzmann-weighted CCS values, based on the 15 initial geometries of PFCA homodimers.

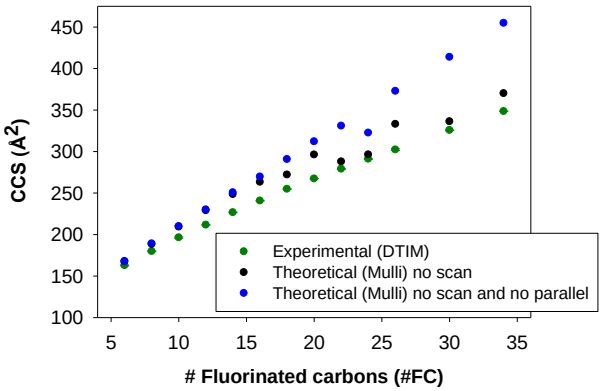


Table S7. Percentage difference between the predicted and DTIM experimental CCS values for homodimeric PFCA ions.

	m/z (M-H)	M06-2X 6-31+G(d,p) **Mulliken**	M06-2X 6-31+G(d,p) **NBO**	M06-2X 6-311++G(d,p) **Mulliken**	M06-2X 6-311++G(d,p) **NBO**
C4-C4	426.9657	+1.84	+1.46	+1.49	+1.22
C5-C5	526.9593	+3.88	+3.41	+3.56	+2.94
C6-C6	626.9529	+4.71	+4.13	+4.56	+3.85
C7-C7	726.9465	+2.69	+1.53	+1.16	-0.38
C8-C8	826.9401	+1.67	+0.67	-2.89	-4.91
C9-C9	926.9337	+1.64	+0.39	-1.26	-3.39
C10-C10	1026.9273	+1.86	+1.05	+2.00	-3.11
C11-C11	1126.9210	+2.76	+1.44	+1.60	-3.32
C12-C12	1226.9146	+2.07	+1.28	+3.26	-1.13
C13-C13	1326.9082	+1.97	-0.05	+2.53	-1.52
C14-C14	1426.9018	+1.84	+1.46	+2.55	+0.71
C16-C16	1626.8890				
C18-C18	1826.8762	+5.80	+4.98		

Figure S13. Structure of the lowest-energy conformer for each homodimeric PFCA ion, with a calculated CCS within 2% of experimental values, obtained at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic geometry. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given.

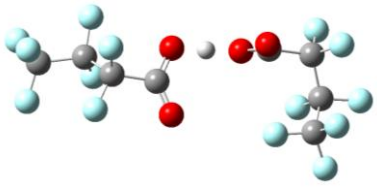
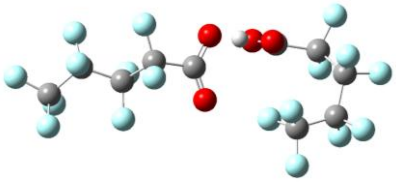
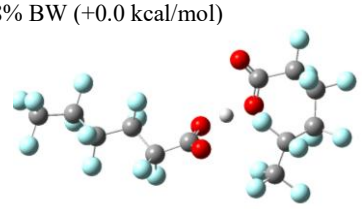
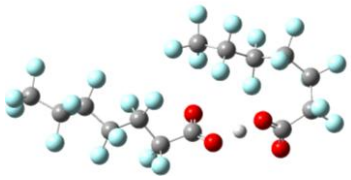
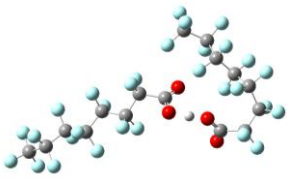
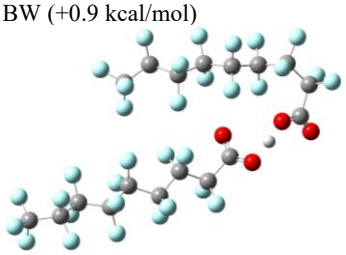
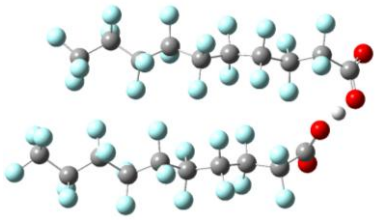
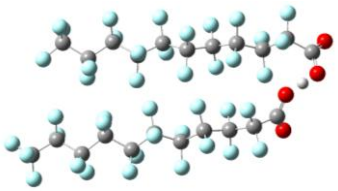
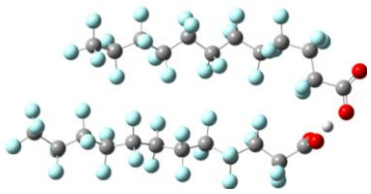
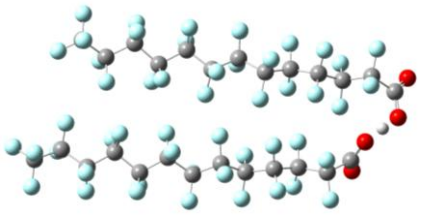
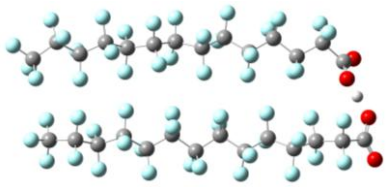
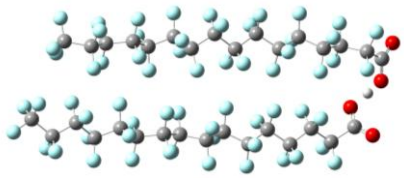
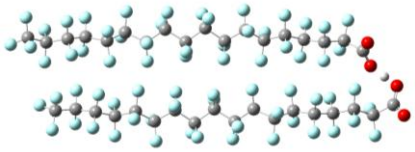
C_4-C_4 (FC = 3-3) 18% BW (+0.1 kcal/mol)  +0.31% (mulli) CF_3-CF_3 = 9.34 Å +0.27% (NBO) Dip = 15.45 D	**C_5-C_5 (FC = 4-4)** 10% BW (+0.8 kcal/mol)  -0.52% (mulli) CF_3-CF_3 = 8.78 Å -1.09% (NBO) Dip = 10.89 D	**C_6-C_6 (FC = 5-5)** 28% BW (+0.0 kcal/mol)  -0.13% (mulli) CF_3-CF_3 = 10.39 Å -1.09% (NBO) Dip = 8.41 D
C_7-C_7 (FC = 6-6) 21% BW (+0.0 kcal/mol)  -1.00% (mulli) CF_3-CF_3 = 8.52 Å -2.97% (NBO) Dip = 28.67 D	**C_8-C_8 (FC = 7-7)** 11% BW (+1.1 kcal/mol)  +1.75% (mulli) CF_3-CF_3 = 12.06 Å -0.45% (NBO) Dip = 12.07 D	**C_9-C_9 (FC = 8-8)** 9% BW (+0.9 kcal/mol)  +0.75% (mulli) CF_3-CF_3 = 8.18 Å -1.67% (NBO) Dip = 21.28 D
C_{10}-C_{10} (FC = 9-9) 53% BW (+0.0 kcal/mol)  +1.55% (mulli) CF_3-CF_3 = 4.76 Å -6.40% (NBO) Dip = 34.39 D	**C_{11}-C_{11} (FC = 10-10)** 23% BW (+0.1 kcal/mol)  +0.73% (mulli) CF3-CF_3 = 6.27 Å -4.17% (NBO) Dip = 35.12 D	**C_{12}-C_{12} (FC = 11-11)** 12% BW (+0.7 kcal/mol)  -1.28% (mulli) CF3-CF_3 = 5.47 Å -1.99% (NBO) Dip = 12.08 D
C_{13}-C_{13} (FC = 12-12) 16% BW (+0.2 kcal/mol)  +0.69% (mulli) CF3-CF_3 = 6.24 Å -0.86% (NBO) Dip = 11.09 D	**C_{14}-C_{14} (FC = 13-13)** 36% BW (+ 0.0 kcal/mol)  +1.46% (mulli) CF3-CF_3 = 4.35 Å -0.67% (NBO) Dip = 8.90 D	**C_{16}-C_{16} (FC = 15-15)** % BW (+ 0.1 kcal/mol)  +4.42% (mulli) CF_3-CF_3 = 4.74 Å +3.83% (NBO) Dip = 8.84 D
C_{18}-C_{18} (FC = 17-17) % BW (+ 0.0 kcal/mol)  +4.00% (mulli) CF3-CF_3 = 5.04 Å +2.33% (NBO) Dip = 11.71 D		

Figure S14. Structure of the lowest-energy conformer for each homodimeric PFCA ion, with a calculated CCS within 2% of experimental values, obtained at the M06-2X/6-31+G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic geometry. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given.

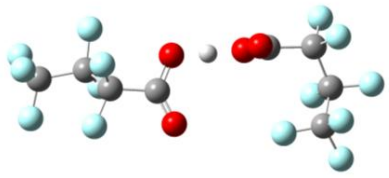
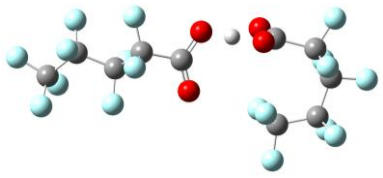
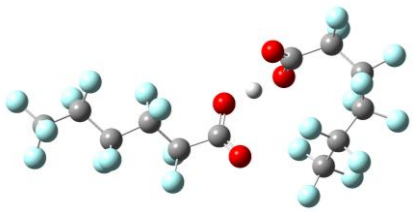
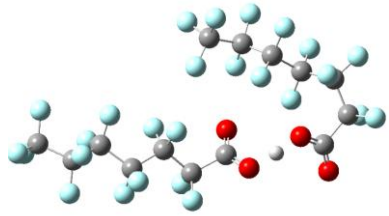
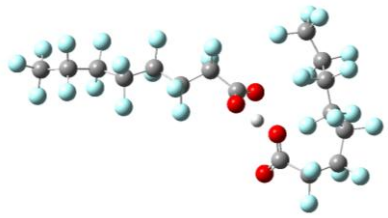
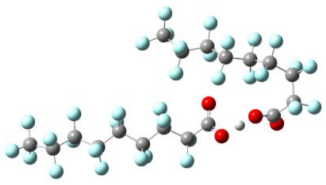
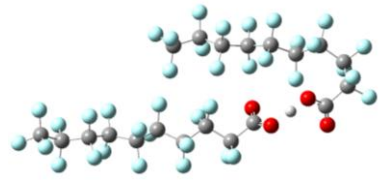
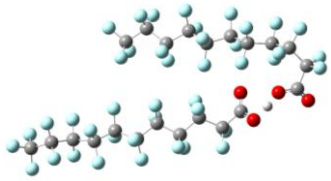
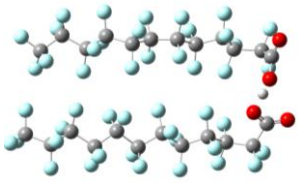
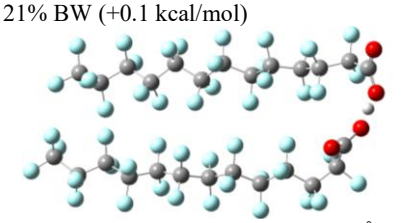
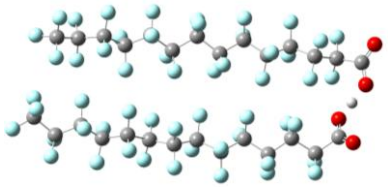
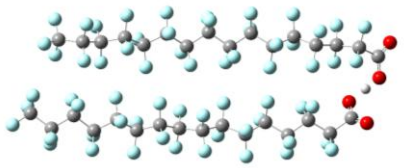
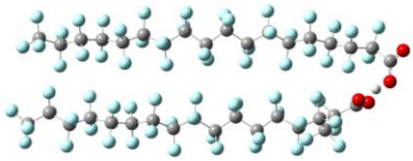
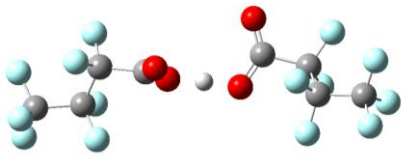
C_4-C_4 (FC = 3-3) 16% BW (+0.0 kcal/mol)  +0.59% (mulli) CF_3-CF_3 = 9.44 Å +0.45% (NBO) Dip = 15.04 D	**C_5-C_5 (FC = 4-4)** 8% BW (+0.7 kcal/mol)  -0.09% (mulli) CF_3-CF_3 = 8.75 Å -0.76% (NBO) Dip = 10.81 D	**C_6-C_6 (FC = 5-5)** 21% BW (+0.0 kcal/mol)  -0.63% (mulli) CF_3-CF_3 = 10.42 Å -1.04% (NBO) Dip = 7.99 D
C_7-C_7 (FC = 6-6) 13% BW (+0.1 kcal/mol)  +0.24% (mulli) CF_3-CF_3 = 8.33 Å -1.58% (NBO) Dip = 13.95 D	**C_8-C_8 (FC = 7-7)** 34% BW (+0.0 kcal/mol)  +0.74% (mulli) CF_3-CF_3 = 12.24 Å -0.31% (NBO) Dip = 11.88 D	**C_9-C_9 (FC = 8-8)** 17% BW (+0.4 kcal/mol)  +1.19% (mulli) CF_3-CF_3 = 9.99 Å +0.27% (NBO) Dip = 27.94 D
C_{10}-C_{10} (FC = 9-9) 70% BW (+0.0 kcal/mol)  +0.53% (mulli) CF_3-CF_3 = 9.47 Å +0.19% (NBO) Dip = 24.35 D	**C_{11}-C_{11} (FC = 10-10)** 54% BW (+0.0 kcal/mol)  +1.05% (mulli) CF_3-CF_3 = 8.58 Å +0.15% (NBO) Dip = 20.99 D	**C_{12}-C_{12} (FC = 11-11)** 2% BW (+2.2 kcal/mol)  +0.31% (mulli) CF3-CF_3 = 4.77 Å -2.65% (NBO) Dip = 31.3 D
C_{13}-C_{13} (FC = 12-12) 21% BW (+0.1 kcal/mol)  +0.94% (mulli) CF3-CF_3 = 5.23 Å -2.27% (NBO) Dip = 31.67 D	**C_{14}-C_{14} (FC = 13-13)** 29% BW (+ 0.1 kcal/mol)  +0.68% (mulli) CF3-CF_3 = 4.51 Å +0.00% (NBO) Dip = 8.62 D	**C_{16}-C_{16} (FC = 15-15)** % BW (+ 1.3 kcal/mol)  +2.70% (mulli) CF_3-CF_3 = 4.77 Å +1.37% (NBO) Dip = 8.91 D
C_{18}-C_{18} (FC = 17-17) % BW (+ kcal/mol)  +4.01% (mulli) CF3-CF_3 = 5.43 Å +1.88% (NBO) Dip = 31.10 D		

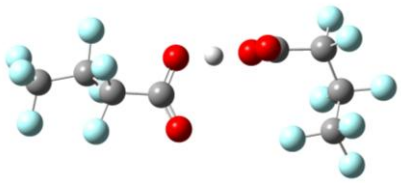
Figure S15. Structures of the ten conformers of the C_4-C_4 PFCA dimer studied at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

#1
24% BW (+0.0 kcal/mol)



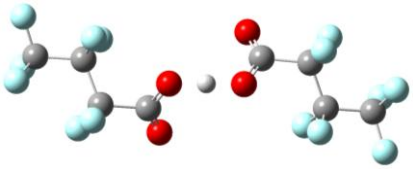
+2.38% (mulli) CF_3-CF_3 = 10.92 Å
+2.55% (NBO) Dip = 13.74 D

#2
18% BW (+0.1 kcal/mol)



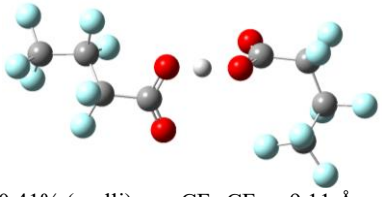
+0.31% (mulli) CF_3-CF_3 = 9.34 Å
+0.27% (NBO) Dip = 15.45 D

#3
18% BW (+0.1 kcal/mol)



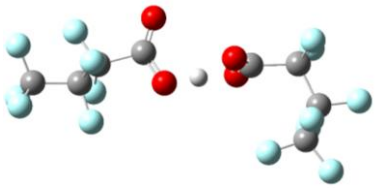
+3.28% (mulli) CF_3-CF_3 = 9.34 Å
+2.02% (NBO) Dip = 15.45 D

#4
11% BW (+0.4 kcal/mol)



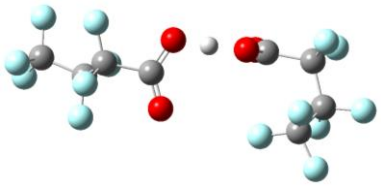
+0.41% (mulli) CF_3-CF_3 = 9.11 Å
+0.09% (NBO) Dip = 13.65 D

#5
8% BW (+0.5 kcal/mol)



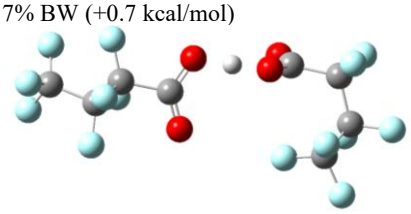
+2.81% (mulli) CF_3-CF_3 = 9.20 Å
+2.44% (NBO) Dip = 13.04 D

#6
7% BW (+0.7 kcal/mol)



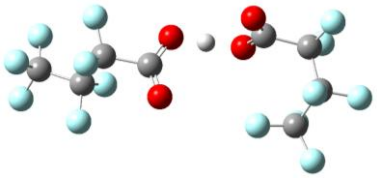
-0.53% (mulli) CF_3-CF_3 = 8.96 Å
-0.66% (NBO) Dip = 7.88 D

#7
7% BW (+0.7 kcal/mol)



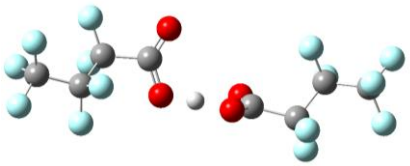
-0.21% (mulli) CF_3-CF_3 = 8.92 Å
-0.13% (NBO) Dip = 7.24 D

#8
6% BW (+0.7 kcal/mol)



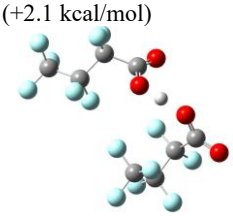
+1.13% (mulli) CF_3-CF_3 = 8.78 Å
+0.69% (NBO) Dip = 30.98 D

#9
4% BW (+1.0 kcal/mol)



+1.38% (mulli) CF3-CF_3 = 11.24 Å
+2.37% (NBO) Dip = 13.46 D

#10
1% BW (+2.1 kcal/mol)



-3.00% (mulli) CF3-CF_3 = 6.22 Å
-3.29% (NBO) Dip = 18.03 D

Figure S16. Structures of the ten conformers of the C_6-C_6 PFCA dimer studied at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

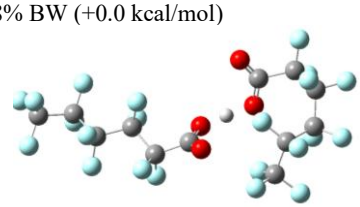
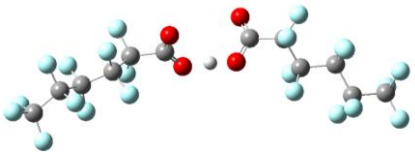
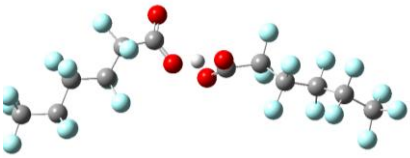
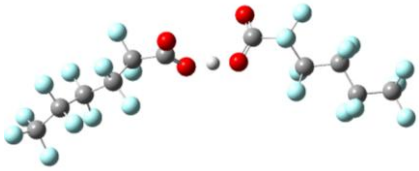
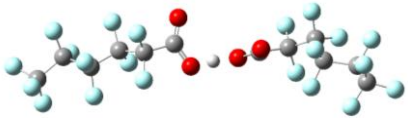
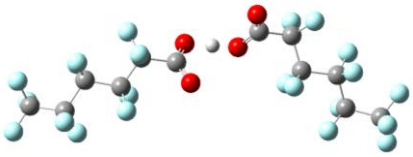
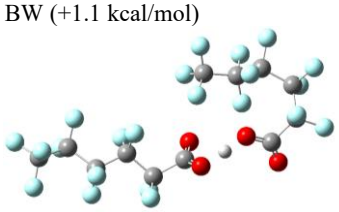
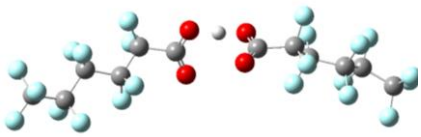
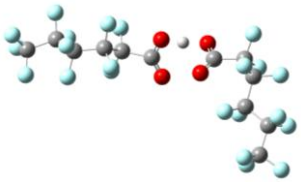
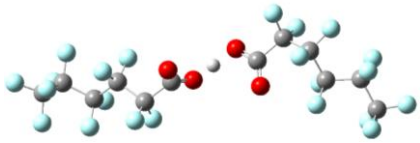
#1 28% BW (+0.0 kcal/mol)  -0.13% (mulli) CF_3-CF_3 = 10.39 Å -1.09% (NBO) Dip = 8.41 D	**#2** 23% BW (+0.1 kcal/mol)  +7.24% (mulli) CF_3-CF_3 = 15.75 Å +6.98% (NBO) Dip = 9.47 D	**#3** 21% BW (+0.2 kcal/mol)  +6.82% (mulli) CF_3-CF_3 = 15.18 Å +6.16% (NBO) Dip = 5.06 D
#4 6% BW (+1.0 kcal/mol)  +6.70% (mulli) CF_3-CF_3 = 15.55 Å +6.82% (NBO) Dip = 7.23 D	**#5** 5% BW (+1.0 kcal/mol)  +7.38% (mulli) CF_3-CF_3 = 15.25 Å +6.04% (NBO) Dip = 13.43 D	**#6** 5% BW (+1.1 kcal/mol)  +7.34% (mulli) CF_3-CF_3 = 15.05 Å +6.03% (NBO) Dip = 6.92 D
#7 5% BW (+1.1 kcal/mol)  -1.69% (mulli) CF_3-CF_3 = 8.11 Å -2.99% (NBO) Dip = 29.73 D	**#8** 3% BW (+1.3 kcal/mol)  +6.41% (mulli) CF_3-CF_3 = 15.37 Å +5.40% (NBO) Dip = 4.83 D	**#9** 4% BW (+1.0 kcal/mol)  +5.62% (mulli) CF3-CF_3 = 13.04 Å +5.35% (NBO) Dip = 7.27 D
#10 1% BW (+1.9 kcal/mol)  +6.27% (mulli) CF3-CF_3 = 15.25 Å +5.70% (NBO) Dip = 13.43 D		

Figure S17. Structures of the ten conformers of the C_8-C_8 PFCA dimer studied at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

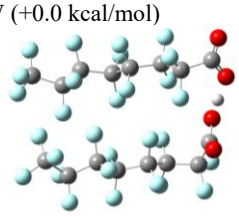
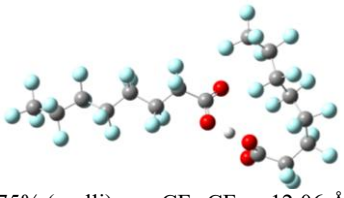
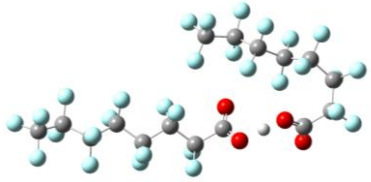
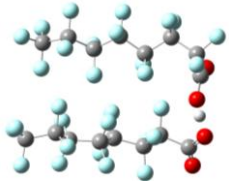
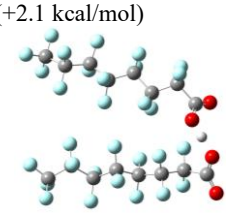
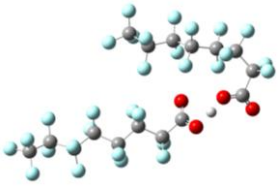
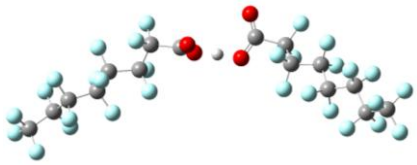
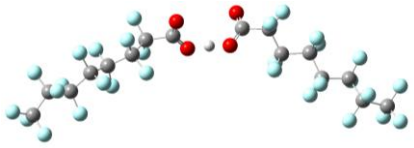
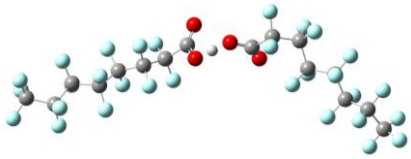
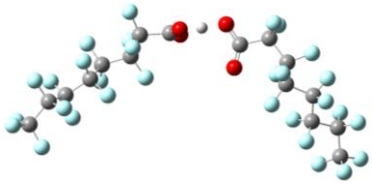
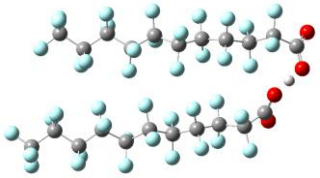
#1 72% BW (+0.0 kcal/mol)  -4.54% (mulli) CF_3-CF_3 = 5.15 Å -6.50% (NBO) Dip = 10.36 D	**#2** 11% BW (+1.1 kcal/mol)  +1.75% (mulli) CF_3-CF_3 = 12.06 Å -0.45% (NBO) Dip = 12.07 D	**#3** 7% BW (+1.4 kcal/mol)  +1.14% (mulli) CF_3-CF_3 = 9.35 Å -0.87% (NBO) Dip = 27.98 D
#4 4% BW (+1.7 kcal/mol)  -3.42% (mulli) CF_3-CF_3 = 5.18 Å -5.83% (NBO) Dip = 9.37 D	**#5** 2% BW (+2.1 kcal/mol)  +0.61% (mulli) CF_3-CF_3 = 6.96 Å -2.25% (NBO) Dip = 11.43 D	**#6** 2% BW (+2.2 kcal/mol)  -0.24% (mulli) CF_3-CF_3 = 6.96 Å -1.91% (NBO) Dip = 11.43 D
#7 1% BW (+2.5 kcal/mol)  +11.8% (mulli) CF_3-CF_3 = 19.30 Å +10.1% (NBO) Dip = 8.23 D	**#8** <1% BW (+3.1 kcal/mol)  +11.7% (mulli) CF_3-CF_3 = 19.63 Å +11.2% (NBO) Dip = 6.97 D	**#9** <1% BW (+3.6 kcal/mol)  +11.8% (mulli) CF3-CF_3 = 19.2 Å +10.2% (NBO) Dip = 12.98 D
#10 <1% BW (+3.7 kcal/mol)  +11.3% (mulli) CF3-CF_3 = 16.67 Å +9.09% (NBO) Dip = 9.63 D		

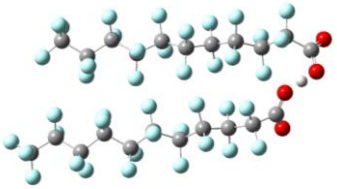
Figure S18. Structures of the ten conformers of the C_{11}-C_{11} PFCA dimer studied at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

#1
26% BW (+0.0 kcal/mol)



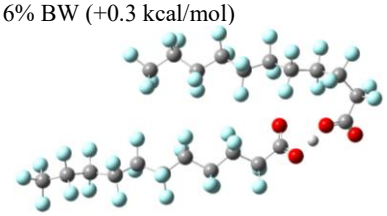
+3.76% (mulli) CF_3-CF_3 = 6.44 Å
-3.68% (NBO) Dip = 34.13 D

#2
20% BW (+0.2 kcal/mol)



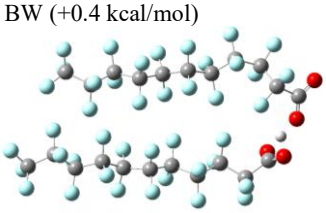
+0.73% (mulli) CF_3-CF_3 = 6.27 Å
-4.17% (NBO) Dip = 35.12 D

#3
16% BW (+0.3 kcal/mol)



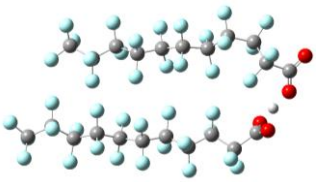
+2.59% (mulli) CF_3-CF_3 = 8.26 Å
-0.77% (NBO) Dip = 21.07 D

#4
14% BW (+0.4 kcal/mol)



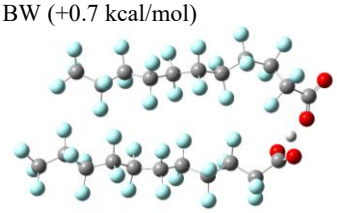
-0.44% (mulli) CF_3-CF_3 = 5.76 Å
-4.73% (NBO) Dip = 10.22 D

#5
8% BW (+0.7 kcal/mol)



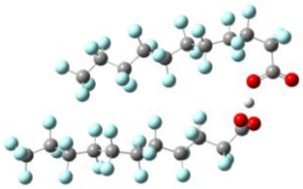
+0.14% (mulli) CF_3-CF_3 = 5.75 Å
-3.57% (NBO) Dip = 11.97 D

#6
8% BW (+0.7 kcal/mol)



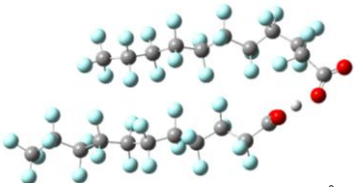
+0.11% (mulli) CF_3-CF_3 = 5.75 Å
-3.69% (NBO) Dip = 11.90 D

#7
5% BW (+1.1 kcal/mol)



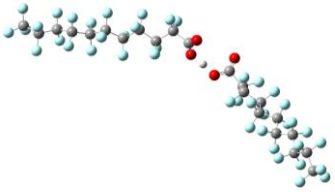
+1.48% (mulli) CF_3-CF_3 = 5.64 Å
-1.89% (NBO) Dip = 30.19 D

#8
3% BW (+1.3 kcal/mol)



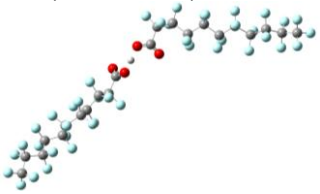
-1.35% (mulli) CF_3-CF_3 = 6.28 Å
-4.35% (NBO) Dip = 33.16 D

#9
<1% BW (+2.7 kcal/mol)



+18.9% (mulli) CF3-CF_3 = 26.49 Å
+16.8% (NBO) Dip = 9.51 D

#10
<1% BW (+4.0 kcal/mol)



+19.0% (mulli) CF3-CF_3 = 26.06 Å
+17.1% (NBO) Dip = 15.94 D

Figure S19. Structures of the ten conformers of the C_{14}-C_{14} PFCA dimer studied at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

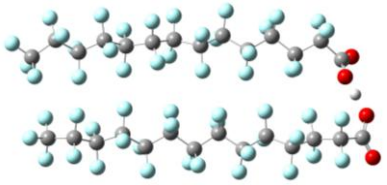
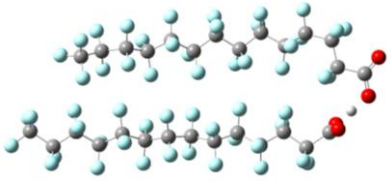
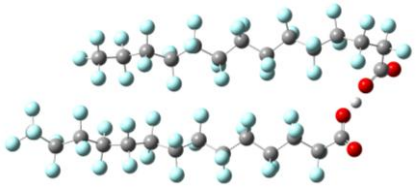
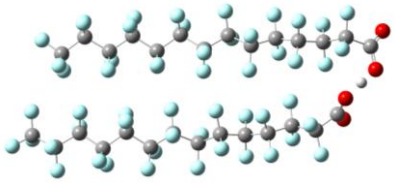
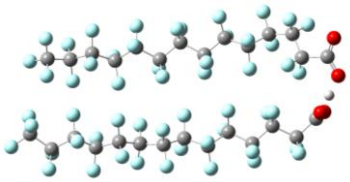
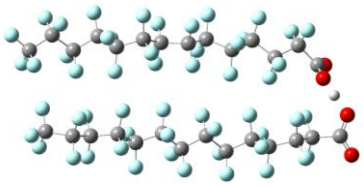
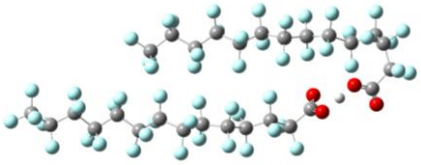
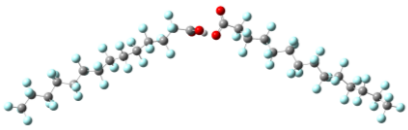
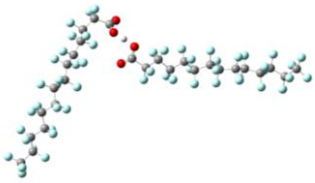
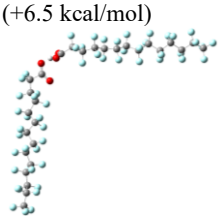
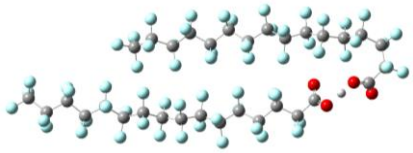
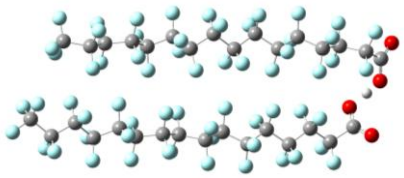
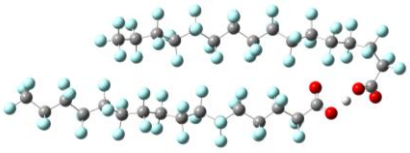
#1 36% BW (+0.0 kcal/mol)  +1.46% (mulli) CF_3-CF_3 = 4.35 Å -0.67% (NBO) Dip = 8.90 D	**#2** 30% BW (+0.1 kcal/mol)  +2.76% (mulli) CF_3-CF_3 = 5.16 Å +2.76% (NBO) Dip = 8.86 D	**#3** 17% BW (+0.4 kcal/mol)  +4.64% (mulli) CF_3-CF_3 = 5.47 Å +1.37% (NBO) Dip = 25.15 D
#4 7% BW (+0.9 kcal/mol)  +1.47% (mulli) CF_3-CF_3 = 4.70 Å -1.38% (NBO) Dip = 33.34 D	**#5** 5% BW (+1.2 kcal/mol)  +2.96% (mulli) CF_3-CF_3 = 4.50 Å -1.00% (NBO) Dip = 31.50 D	**#6** 4% BW (+1.3 kcal/mol)  +2.33% (mulli) CF_3-CF_3 = 4.51 Å +0.12% (NBO) Dip = 8.07 D
#7 1% BW (+2.4 kcal/mol)  +7.19% (mulli) CF_3-CF_3 = 4.70 Å +3.44% (NBO) Dip = 33.34 D	**#8** <1% BW (+5.2 kcal/mol)  +40.21 (mulli) CF_3-CF_3 = 33.02 Å +24.12% (NBO) Dip = 11.68 D	**#9** <1% BW (+5.5 kcal/mol)  +20.0% (mulli) CF_3-CF_3 = 27.59 Å +19.7% (NBO) Dip = 7.88 D
#10 <1% BW (+6.5 kcal/mol)  +22.9% (mulli) CF3-CF_3 = 28.16 Å +22.4% (NBO) Dip = 11.93 D		

Figure S20. Structures of the ten conformers of the C_{18}-C_{18} PFCA dimer studied at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

#1 % BW (+0.0 kcal/mol)  +6.96% (mulli) CF_3-CF_3 = 7.91 Å +3.24% (NBO) Dip = 38.68 D	**#2** % BW (+0.1 kcal/mol)  +4.42% (mulli) CF_3-CF_3 = 4.74 Å +0.86% (NBO) Dip = 8.84 D	**#3** % BW (+0.6 kcal/mol)  +5.92% (mulli) CF_3-CF_3 = 7.15 Å +6.94% (NBO) Dip = 20.94 D
#4 % BW (+ kcal/mol) -% (mulli) CF_3-CF_3 = Å -% (NBO) Dip = D	**#5** % BW (+ kcal/mol) -% (mulli) CF_3-CF_3 = Å -% (NBO) Dip = D	**#6** % BW (+ kcal/mol) -% (mulli) CF_3-CF_3 = Å -% (NBO) Dip = D
#7 % BW (+ kcal/mol) -% (mulli) CF_3-CF_3 = Å -% (NBO) Dip = D	**#8** % BW (+ kcal/mol) -% (mulli) CF_3-CF_3 = Å -% (NBO) Dip = D	**#9** % BW (+ kcal/mol) -% (mulli) CF_3-CF_3 = Å -% (NBO) Dip = D
#10 % BW (+ kcal/mol) -% (mulli) CF_3-CF_3 = Å -% (NBO) Dip = D		

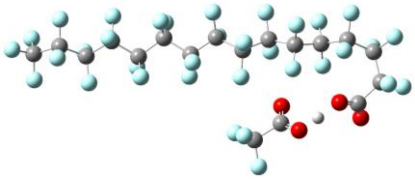
3.5. Results for PFCA asymmetrical isobaric dimeric ions

Table S8. Percentage difference between the predicted and DTIM experimental CCS values for PFCA asymmetrical isobaric dimeric ions.

	# Fluorinated carbon atoms in each chain	M06-2X 6-31+G(d,p) **Mulliken**	M06-2X 6-31+G(d,p) **NBO**	M06-2X 6-311++G(d,p) **Mulliken**	M06-2X 6-311++G(d,p) **NBO**
C2-C16	1-15	+0.79	+0.00	+1.10	-0.83
C4-C14	3-13	-1.55	-3.19	-1.25	-3.80
C5-C13	4-12	-1.24	-3.36	-0.79	-4.33
C6-C12	5-11	-1.29	-3.20	-1.18	-4.93
C7-C11	6-10	+0.16	-2.01	-0.01	-4.23
C8-C10	7-9	-0.01	-0.90	-1.67	-3.66
C9-C9	8-8	+1.63	+0.39	-1.26	-3.39

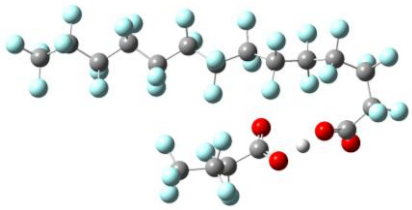
Figure S21. Structure of the lowest-energy conformer for each PFCA asymmetrical isobaric dimeric ion, with a calculated CCS within 2% of experimental values, obtained at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic geometry. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. The bolded box highlights the geometry with less than 2% error with Mulliken descriptors.

C_2-C_{16} (FC = 1-15)
32% BW (+0.0 kcal/mol)



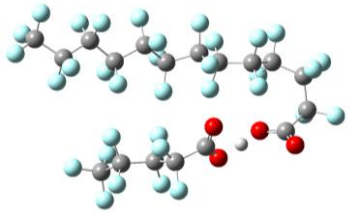
+1.13% (mulli) CF_3-CF_3 = 11.67 Å
-0.34% (NBO) Dip = 24.51 D

C_4-C_{14} (FC = 3-13)
33% BW (+0.0 kcal/mol)



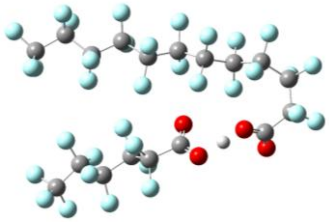
-1.89% (mulli) CF_3-CF_3 = 8.05 Å
-4.68% (NBO) Dip = 31.84 D

C_5-C_{13} (FC = 4-12)
49% BW (+0.0 kcal/mol)



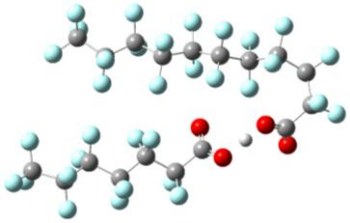
+0.08% (mulli) CF_3-CF_3 = 7.89 Å
-3.91% (NBO) Dip = 16.74 D

C_6-C_{12} (FC = 5-11)
16% BW (+0.7 kcal/mol)



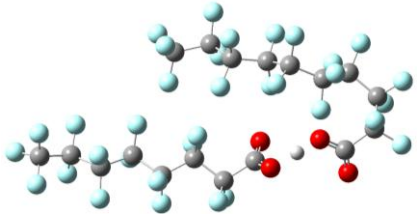
-1.01% (mulli) CF_3-CF_3 = 6.62 Å
-4.01% (NBO) Dip = 27.57 D

C_7-C_{11} (FC = 6-10)
36% BW (+0.0 kcal/mol)



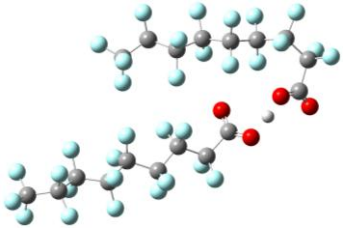
-0.08% (mulli) CF_3-CF_3 = 6.50 Å
-4.78% (NBO) Dip = 27.91 D

C_8-C_{10} (FC = 7-9)
22% BW (+0.4 kcal/mol)



-0.03% (mulli) CF_3-CF_3 = 7.47 Å
-3.07% (NBO) Dip = 27.79 D

C_9-C_9 (FC = 8-8)
9% BW (+0.9 kcal/mol)



+0.75% (mulli) CF_3-CF_3 = 8.18 Å
-1.67% (NBO) Dip = 21.28 D

Figure S22. Structure of the lowest-energy conformer for each PFCA asymmetrical isobaric dimeric ion, with a calculated CCS within 2% of experimental values, obtained at the M06-2X/6-31+G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic geometry. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. The bolded box highlights the geometry with less than 2% error with Mulliken descriptors.

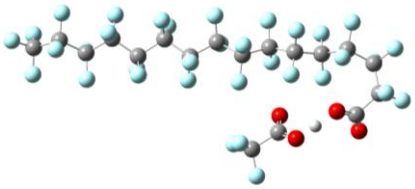
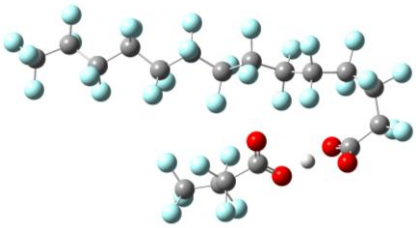
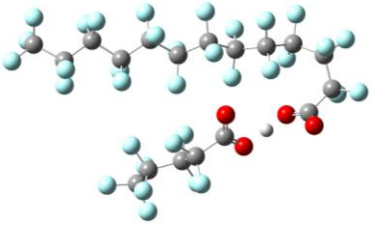
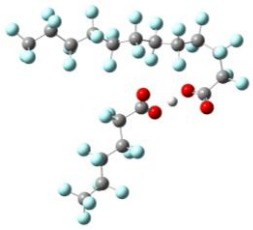
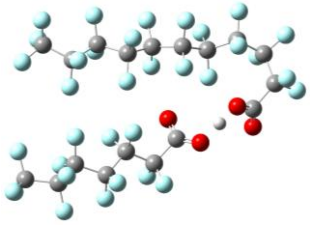
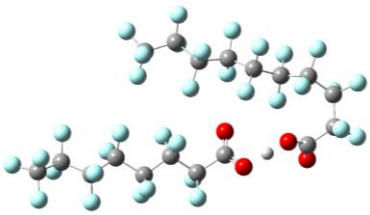
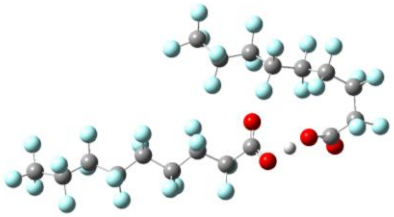
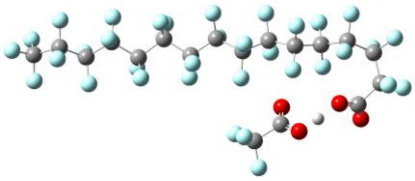
<table>
<tr>
<td>C_2-C_{16} (FC = 1-15)
30% BW (+0.0 kcal/mol)
 
+0.74% (mulli) CF_3-CF_3 = 11.89 Å
+0.27% (NBO) Dip = 24.56 D</td>
<td>C_4-C_{14} (FC = 3-13)
29% BW (+0.0 kcal/mol)
 
-1.73% (mulli) CF_3-CF_3 = 8.23 Å
-3.33% (NBO) Dip = 16.85 D</td>
<td>C_5-C_{13} (FC = 4-12)
41% BW (+0.0 kcal/mol)
 
-1.62% (mulli) CF_3-CF_3 = 8.21 Å
-3.16% (NBO) Dip = 16.83 D</td>
</tr>
<tr>
<td>C_6-C_{12} (FC = 5-11)
21% BW (+0.3 kcal/mol)
 
+1.10% (mulli) CF_3-CF_3 = 9.99 Å
-1.45% (NBO) Dip = 23.13 D</td>
<td>C_7-C_{11} (FC = 6-10)
27% BW (+0.0 kcal/mol)
 
-1.89% (mulli) CF_3-CF_3 = 6.76 Å
-4.16% (NBO) Dip = 27.90 D</td>
<td>C_8-C_{10} (FC = 7-9)
32% BW (+0.0 kcal/mol)
 
-1.93% (mulli) CF_3-CF_3 = 7.71Å
-2.53% (NBO) Dip = 27.79 D</td>
</tr>
<tr>
<td>C_9-C_9 (FC = 8-8)
17% BW (+0.4 kcal/mol)
 
+1.19% (mulli) CF_3-CF_3 = 9.99 Å
+0.27% (NBO) Dip = 27.94 D</td>
<td></td>
<td></td>
</tr>
</table>

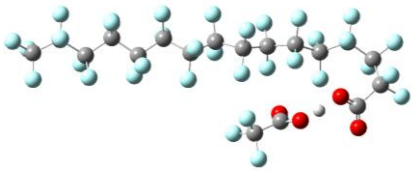
Figure S23. Structures of the ten conformers of the C_2-C_{16} PFCA dimer studied at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

#1
32% BW (+0.0 kcal/mol)



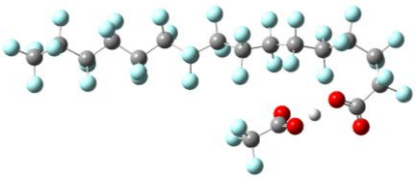
+1.13% (mulli) CF_3-CF_3 = 11.67 Å
-0.34% (NBO) Dip = 24.51 D

#2
29% BW (+0.1 kcal/mol)



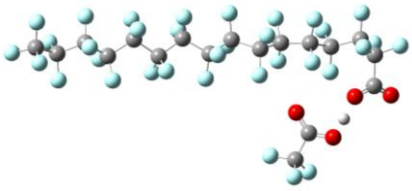
+0.54% (mulli) CF_3-CF_3 = 11.63 Å
-0.72% (NBO) Dip = 24.54 D

#3
29% BW (+0.1 kcal/mol)



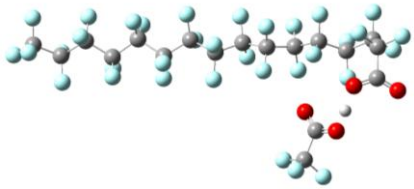
+1.13% (mulli) CF_3-CF_3 = 11.65 Å
-2.56% (NBO) Dip = 26.70 D

#4
2% BW (+1.7 kcal/mol)



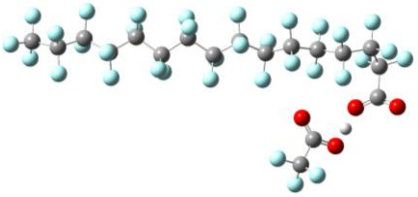
+3.11% (mulli) CF_3-CF_3 = 14.76 Å
+2.91% (NBO) Dip = 19.69 D

#5
2% BW (+1.7 kcal/mol)



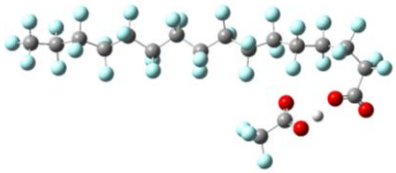
+3.05% (mulli) CF_3-CF_3 = 14.71 Å
+2.89% (NBO) Dip = 29.45 D

#6
2% BW (+1.7 kcal/mol)



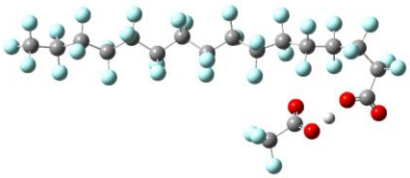
+3.81% (mulli) CF_3-CF_3 = 14.73 Å
+3.88% (NBO) Dip = 14.47 D

#7
2% BW (+1.8 kcal/mol)



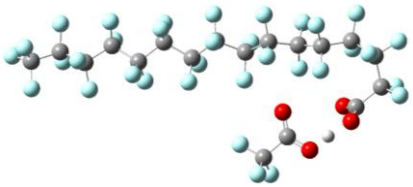
+1.41% (mulli) CF_3-CF_3 = 4.70 Å
+0.35% (NBO) Dip = 33.34 D

#8
2% BW (+1.8 kcal/mol)



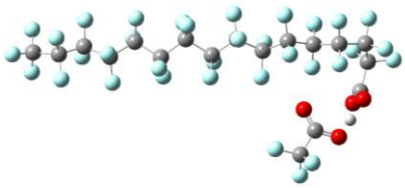
+1.12% (mulli) CF_3-CF_3 = 13.13Å
+0.72% (NBO) Dip = 29.97 D

#9
1% BW (+2.1 kcal/mol)



+0.79% (mulli) CF_3-CF_3 = 12.27 Å
-0.07% (NBO) Dip = 34.30 D

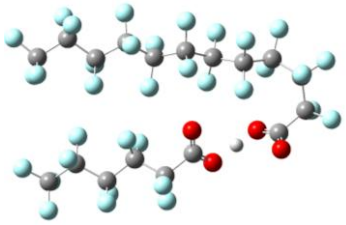
#10
1% BW (+2.3 kcal/mol)



+3.12% (mulli) CF3-CF_3 = 14.56 Å
+2.77% (NBO) Dip = 30.15 D

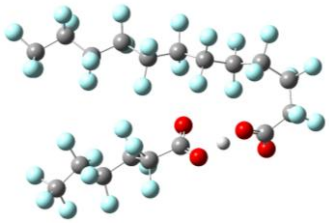
Figure S24. Structures of the ten conformers of the C_6-C_{12} PFCA dimer studied at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

#1
48% BW (+0.0 kcal/mol)



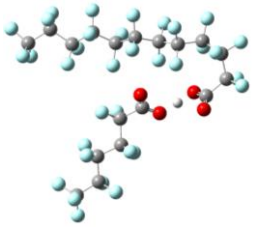
-3.07% (mulli) CF_3-CF_3 = 5.69 Å
-6.54% (NBO) Dip = 17.79 D

#2
16% BW (+0.7 kcal/mol)



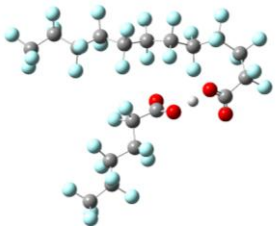
-1.01% (mulli) CF_3-CF_3 = 6.62 Å
-4.01% (NBO) Dip = 27.57 D

#3
13% BW (+0.8 kcal/mol)



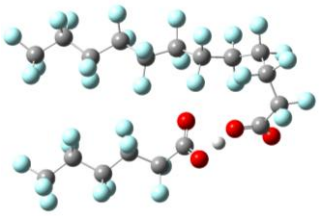
+3.12% (mulli) CF_3-CF_3 = 9.38 Å
-2.47% (NBO) Dip = 23.40 D

#4
12% BW (+0.9 kcal/mol)



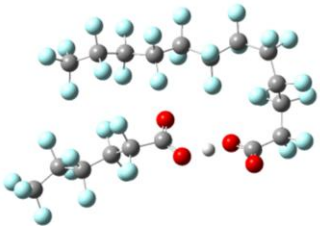
+2.75% (mulli) CF_3-CF_3 = 9.36 Å
-2.23% (NBO) Dip = 24.76 D

#5
6% BW (+1.3 kcal/mol)



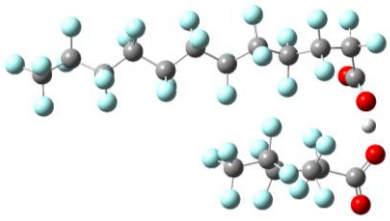
-4.07% (mulli) CF_3-CF_3 = 5.64 Å
-6.78% (NBO) Dip = 31.56 D

#6
3% BW (+1.8 kcal/mol)



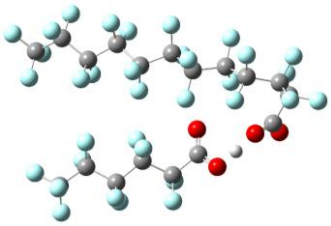
-3.34% (mulli) CF_3-CF_3 = 6.33 Å
-5.46% (NBO) Dip = 13.59 D

#7
2% BW (+2.0 kcal/mol)



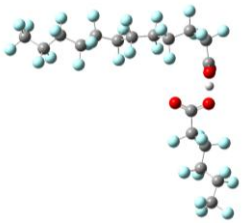
+1.65% (mulli) CF_3-CF_3 = 8.86 Å
-0.90% (NBO) Dip = 10.77 D

#8
<1% BW (+2.9 kcal/mol)



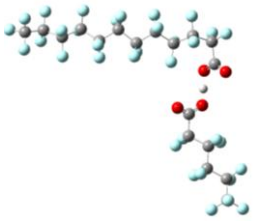
+0.07% (mulli) CF_3-CF_3 = 6.27 Å
-5.18% (NBO) Dip = 32.76 D

#9
<1% BW (+3.1 kcal/mol)



+10.17% (mulli) CF_3-CF_3 = 17.23 Å
+8.05% (NBO) Dip = 16.02 D

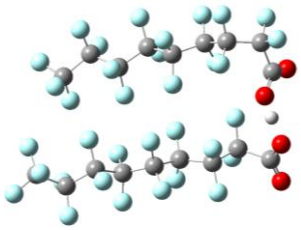
#10
<1% BW (+3.6 kcal/mol)



+10.56% (mulli) CF3-CF_3 = 18.19 Å
+9.23% (NBO) Dip = 15.90 D

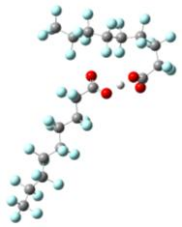
Figure S25. Structures of the ten conformers of the C_9-C_9 PFCA dimer studied at the M06-2X/6-311++G(d,p) level of theory. The Boltzmann weight is given, along with the energy difference with the least energetic conformer. The CCS deviation from DTIM experimental values is expressed for the Mulliken (mulli) and NBO partial charge description, and the F_3C-CF_3 distance and dipolar moment are also given. Bolded boxes highlight the conformers with less than 2% error with Mulliken descriptors.

#1
41% BW (+0.0 kcal/mol)



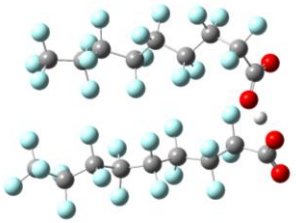
-4.98% (mulli) CF_3-CF_3 = 4.71 Å
-6.04% (NBO) Dip = 44.45 D

#2
14% BW (+0.7 kcal/mol)



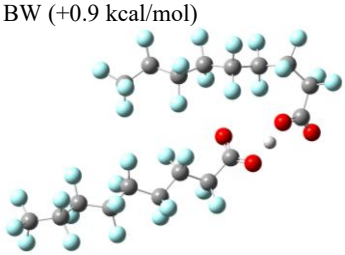
+5.84% (mulli) CF_3-CF_3 = 13.62 Å
+2.36% (NBO) Dip = 23.85 D

#3
12% BW (+0.7 kcal/mol)



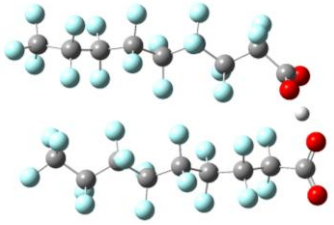
-2.50% (mulli) CF_3-CF_3 = 5.21 Å
-5.35% (NBO) Dip = 44.16 D

#4
9% BW (+0.9 kcal/mol)



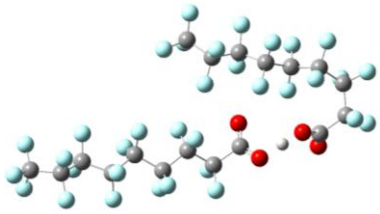
+0.75% (mulli) CF_3-CF_3 = 8.18 Å
-1.67% (NBO) Dip = 21.28 D

#5
8% BW (+1.0 kcal/mol)



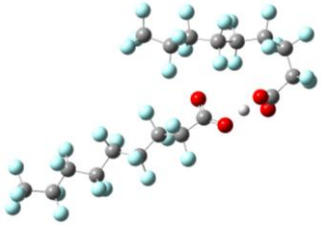
-2.11% (mulli) CF_3-CF_3 = 4.93 Å
-5.54% (NBO) Dip = 43.61 D

#6
8% BW (+1.0 kcal/mol)



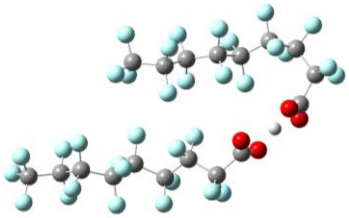
+2.28% (mulli) CF_3-CF_3 = 9.88 Å
-0.03% (NBO) Dip = 27.91 D

#7
5% BW (+1.3 kcal/mol)



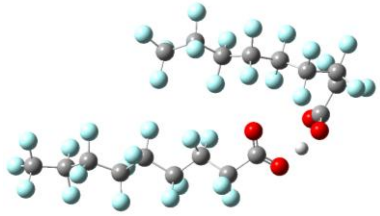
+2.92% (mulli) CF_3-CF_3 = 10.64 Å
-0.68% (NBO) Dip = 27.80 D

#8
2% BW (+1.9 kcal/mol)



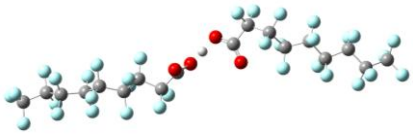
+0.79% (mulli) CF_3-CF_3 = 7.39 Å
-1.98% (NBO) Dip = 21.94 D

#9
1% BW (+2.1 kcal/mol)



+1.21% (mulli) CF_3-CF_3 = 8.26 Å
-1.56% (NBO) Dip = 14.75 D

#10
<1% BW (+3.9 kcal/mol)



+12.87% (mulli) CF3-CF_3 = 22.77 Å
+12.26% (NBO) Dip = 14.84 D

4. References

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