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A crystal engineering utilization of hexafurcated hydrogen bonding to construction of subnano fluorinated tunnels

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Abstract

This report describes a seven centered (hexafurcated) hydrogen bonding system found in the crystals of the trifluorolactates, which construct one dimensional hydrogen bonding network, and a crystal engineering utilization of the network for construction of subnano fluorinated tunnels.

Keywords: Trifluorolactate; Hexafurcated hydrogen bonding system; Hydrogen bonding network; Subnano fluorinated tunnel; Trifluoromethyl group

1. Introduction

Molecular interactions have been controlled by introduction of fluorine atoms into organic compounds. Introduction of fluorine atoms into molecules sometimes results in the formation of "hard" molecule with low electronic polarizability. Unexpected low boiling points of the fluorinated molecules could be explainable by their low electronic polarizabilities [1]. Moreover, the fluorine atom withdraws electrons from other part of the molecule, and thus is somewhat negatively charged [2]. Therefore, the fluorine atoms can participate in electrostatic interactions, such as the weak hydrogen bondings and the coordination to metals [3–33]. These properties of the fluorine atom would give a unique molecular recognizing ability to the fluoro-organics [1].

Previously, we reported a strong chiral recognizing ability of isopropyl trifluorolactate **1b** [34]. The compound **1b** experienced discrimination of its optical purity via a simple distillation process. When 2 g of **1b** with 74% ee was submitted to a distillation, 1 g of 82% ee distillate **1b** and 1 g of 66% ee residue **1b** was obtained. Moreover, boiling points of the enantiomerical mixture of the compound were varied depending on its optical purity. The IR spectra of the compounds having different optical purities with different boiling points suggested some participation of fluorine atoms into this chiral recognition. To date, only one another example on discrimination of optical purity by simple distillation had been reported [35]. The compound is *N*-CF_3CO-Val-OMe, *N*-trifluoroacetylated valine methyl ester, which also has a trifluoromethyl moiety in its structure.

Since our report, the phenomena had been depicted as a remarkable example of nonlinear effect, caused by homo- and hetero-intermolecular interactions [36–38]. Very recently, a successive single proton multicenter hydrogen bonding system was found in the crystal of the trifluorolactates **1a**, **1b**, and **2d**. The hydrogen bonding interactions in the system may explain the phenomena above [39].

In this report, (1) a detailed study on the structures of the hydrogen bonding system, and (2) a crystal engineering study on the construction of subnano sized trifluoromethylated tunnels are described.

2. Multicenter single proton hydrogen bonding and its network structure

The packing with the successive multicenter hydrogen bonding system of the isopropyl trifluorolactate **1b** is illustrated in Fig. 1 [39]. The illustrate reveals that each –OH group of the trifluorolactate bears three inter and three intramolecular hydrogen bondings around it; the –OH group seems to be the center of hexafurcated hydrogen bonding, seven centered hydrogen bonding. Moreover, this hydrogen bonding system constructs a spiral ladder network. The same seven centered hydrogen bonding system was also seen in the crystals of every trifluorolactates **1a**, **1b**, and **2a–g** which

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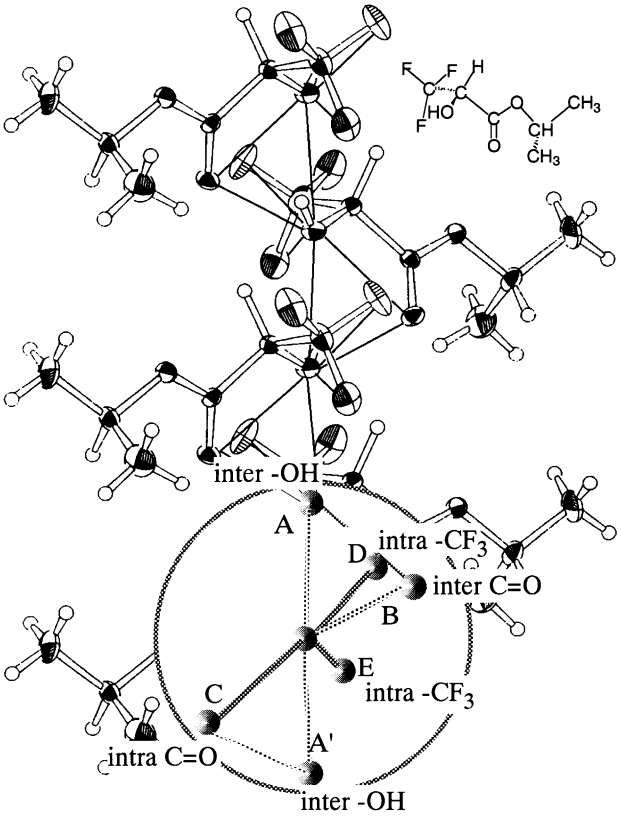


Fig. 1. Hexafurcated hydrogen bonding system in a one dimensional hydrogen bonding network.

we have examined. Table 1 summarizes the distances between center oxygen atom and surrounding hetero-atoms. These distances seem to be independent from the structure of alkyl moieties of the trifluorolactates.

The intermolecular distance of O–O between neighboring –OH groups was found 2.8–2.9 Å (A and A′ in Table 1). The intermolecular distance of O–O between –OH group to C=O was found 2.8–3.1 Å (B in Table 1) and the intramolecular distance of O–O between –OH group to C=O was found 2.6–2.7 Å (C in Table 1). It was reported that the neutron diffraction study on the cyclodextrin hydrates revealed that the possibility of HB with O–O distances shorter than 3.0 Å is 100% [40–42]. Thus, it seems to be sure that one –OH group is hydrogen bonded at least to four oxygen atoms inter and intramolecularly, and possibly to two fluorine atoms intramolecularly. However, this seven centered structure of this hydrogen bonding system is very unusual. The hydroxy function can donate one proton to a hydrogen bond and possesses two oxygen lone pairs as acceptors, thus can participate in three conventional hydrogen bondings at most [43,44]. Actually, three centered, so called bifurcated, hydrogen bondings have often been found in crystals of amino acids and sugars. While, four centered, so called trifurcated, hydrogen bondings are relatively rare, and more than five centered hydrogen bondings are scarce [40–42]. Thus, the hydrogen bonding system found in the trifluorolactates may be based not only on orbital oriented proton exchanges, but also on some coulombic interactions [45].

Table 1
Distances between –OH oxygen and the surrounding hetero-atoms

Compound	Intermolecular [Å]		Intramolecular [Å]		
	A = A′	B	C	D	E
1a	2.8	2.9	2.6	2.7	3.0
1b	2.8	2.9	2.7	2.7	2.8
2a	2.9	3.0	2.6	2.7	2.9
2b	2.8	3.1	2.7	2.6	2.9
2c	2.8	3.0	2.6	2.7	2.9
2d	2.8	2.9	2.6	2.7	2.9
2e	2.8	2.9	2.6	2.7	2.8
2f	2.9	2.8	2.6	2.7	2.8
2g	2.9	2.9	2.6	2.7	2.9

3. Crystal engineering study on the construction of subnano sized trifluoromethylated tunnels

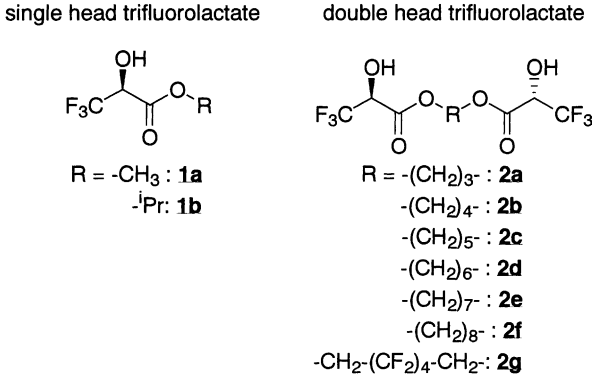
Hydrogen bondings are among the strongest and most directional intermolecular interactions. They play a crucial role in construction and molecular recognition of supramolecular biological systems, such as DNA, transcriptions to RNA, folding of proteins, cell adhesion, etc. Although, such strict recognition needs a big molecule with many functionalities.

Meanwhile, successful artificial molecular recognitions have been mainly done by metal coordination [46,47]. Similarly, the metal coordinations have been widely used for construction of artificial supramolecular cage structures [48,49]. The metal coordination can connect few ligands at once, thus could be used for hinge or bridgehead for supramolecular structures. Meanwhile, the conventional hydrogen bonding usually connects one proton donor by one proton acceptor, thus has been used for just one by one connection of the molecules. Therefore, a unit molecule with many hydrogen bonding functionalities is needed for higher order structures [50–52].

As shown in Fig. 1, the hydrogen bonding network of the single head trifluorolactates **1** connects unit molecules at once to construct infinite hydrogen bonded ribbons in their crystals. Thus, one may expect that the double head trifluorolactates **2** may give an infinite hydrogen bonded sheet in its crystal (Schemes 1 and 2).

The Fig. 2 summarizes the molecular packing view of double head trifluorolactates **2a–g** from the top of the needles. In all these cases, the double head trifluorolactates knot up two dimensional infinite waving sheets by the hydrogen bonding network in their crystals. These crystals are all needles, and their directions were agreed to that of hydrogen bonding networks. That is, the dominating intermolecular force would be caused by the hydrogen bonding network.

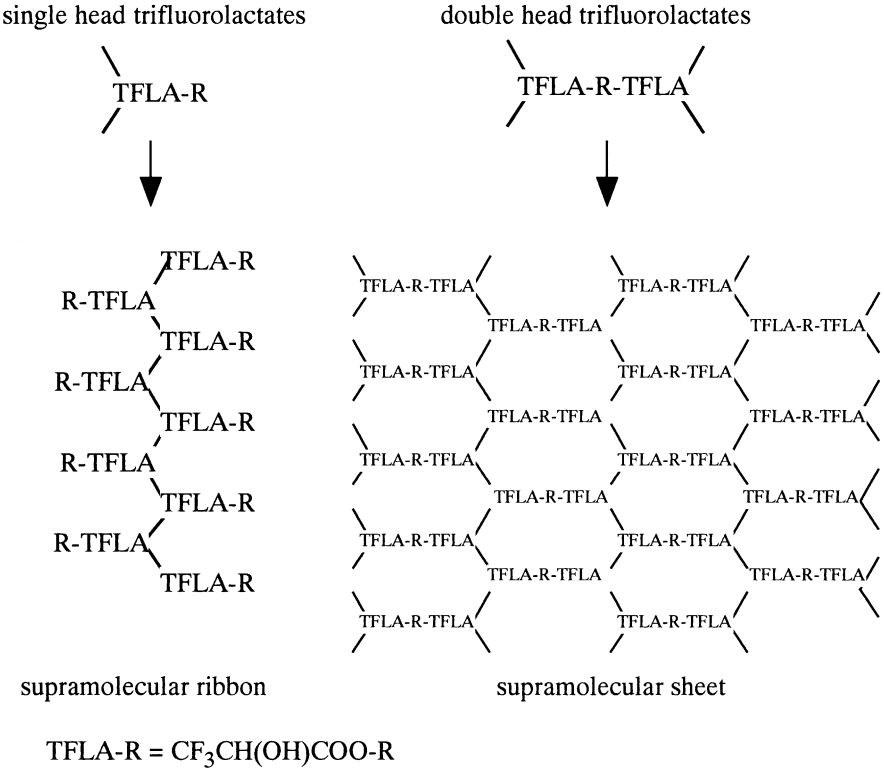
Based on the arrangement of the hydrogen bonding networks and the accumulation of the sheets, we may categorize



Scheme 1.

these crystals into four, which are summarized in Scheme 3. The first is ''cisoid-parallel'', which has cisoid trifluorolactic moieties toward the linker polymethylene, and constructs square wave pattern supramolecular sheets, and the sheets are stacked parallel way. The surface of the sheet is constructed by oligo methylene linker and the gutter (or wall) is constructed by hydrogen bonded trifluorolactate. The double head trifluorolactates connected by hexamethylene **1d** and octamethylene **1f** have this arrangement. The second is ''cisoid-antiparallel'' which has also cisoid trifluorolactic moieties toward the linker polymethylene, and constructs a distorted square wave pattern sheet. The surface of the sheet is constructed by one trifluorolactate with the half of the linker. The double head trifluorolactates connected by trimethylene **1a** has this arrangement. The third is ''transoid-parallel'', which has a conformation of two trifluorolactic moieties toward the linker with the accumulation of the sheets just parallel way. The double head trifluorolactates connected by the tetramethylene **1b**, the pentamethylene **1c** and the heptamethylene **1e**, has this arrangement. All the directions of one dimensional hydrogen bonding networks in crystals of this category are the same. Thus, the needle crystal has macro up and down due to the direction of the hydrogen bonding network. The last is ''transoid-antiparallel'', which has a transoid conformation of the trifluorolactic moieties toward the linker but the sheets are accumulated antiparallel way. This way of accumulation was found in the case of double head trifluorolactate with partially fluorinated linker **1g**, 2,2,3,3,4,4,5,5-octafluorohexamethylene linker, though this category of accumulation of the sheet could not be found in the other double head trifluorolactates with simple methylene linkers.

It is noteworthy that, the two trifluorolactic moieties of **1b** build different hydrogen bonding systems. There seems that two molecule of compound **1b** coupled by conventional 1:1 hydrogen bondings as illustrated in Scheme 4 [43,44]. The both end of this coupled molecules, noted in the circle in Scheme 4, knot up the one dimensional hydrogen bonding network which is shown in Scheme 1. This spontaneous distinction of hydrogen bonding systems in the crystalline symmetrical double head trifluorolactate **1b** implies that the stabilizing energy for the present hydrogen bonding system would be comparable to the sum of the conventional



Scheme 2.

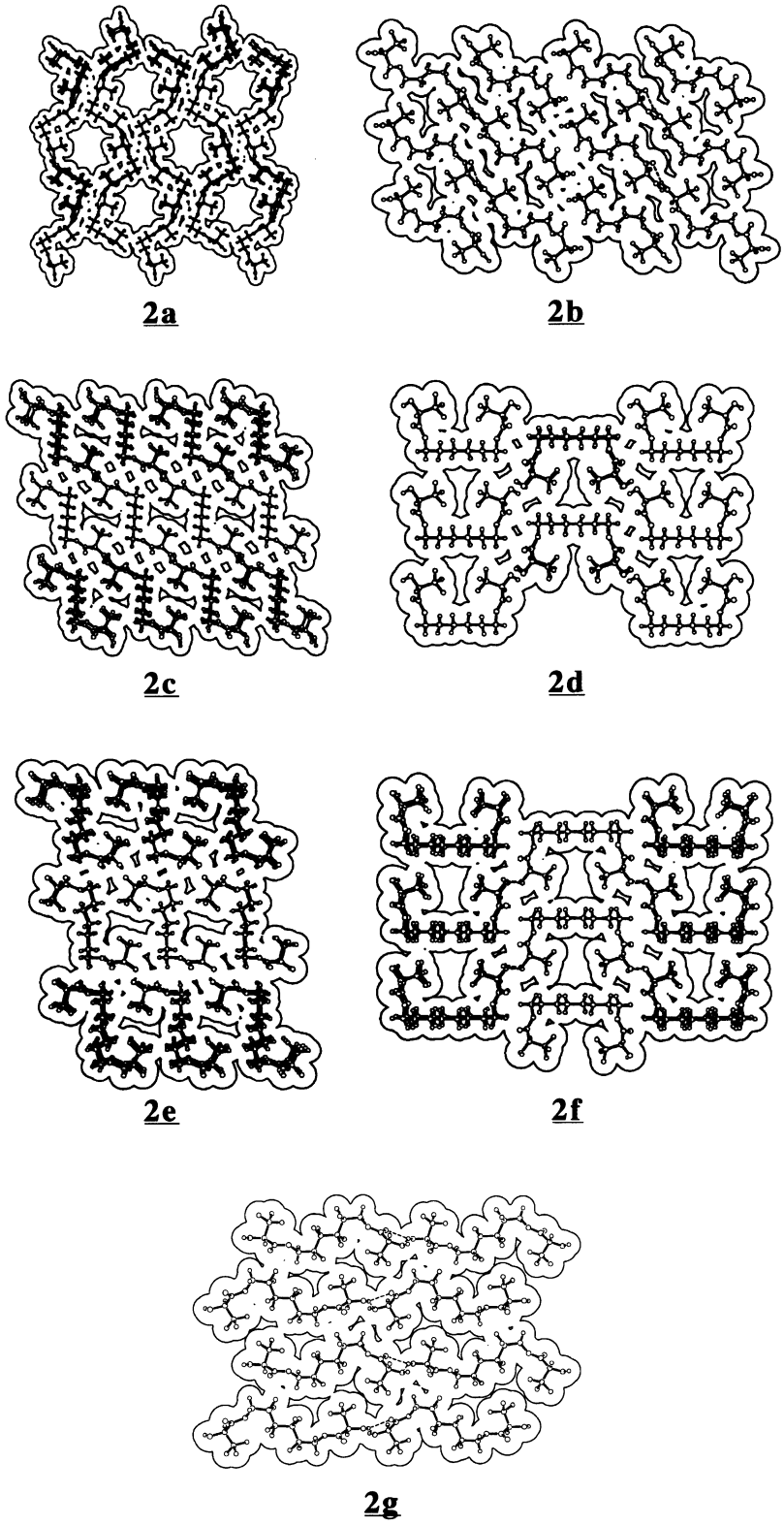
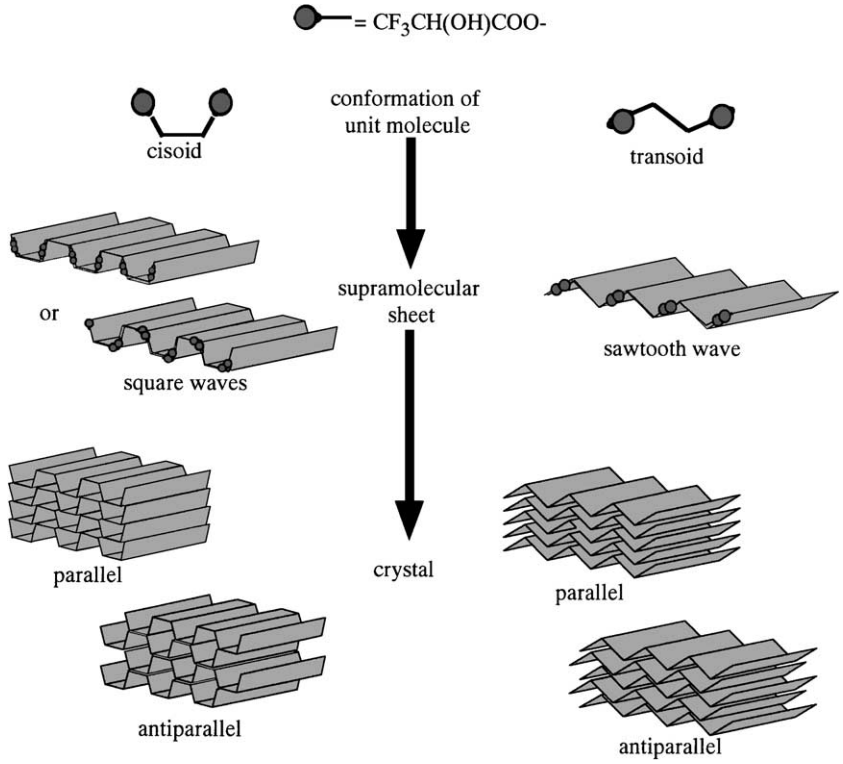


Fig. 2. Packing views of trifluorolactates from the tops of the needles.

multicenter hydrogen systems and the torsion energy of the molecule [43,44].

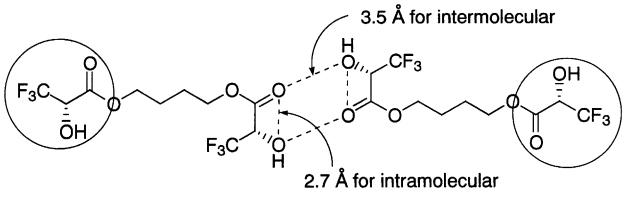
It is obvious that the interactions between the supramolecular sheets of the double head trifluorolactates **2** are that of van der Waals interactions. Of course, the origin of the van der Waals interactions is the electronic polarizability of the molecule, which could be estimated by refractive indices [1]. Moreover, the fluorinated compounds had small refractive



Scheme 3.

indices, in general. Among the moieties of the present molecules, the trifluoromethyl moiety would undertake the smallest van der Waals interactions, and the carbonyloxy moiety, the sole *p*-system, would undertake the largest interactions. Actually, the contact point of the sheets seems to be the carbonyloxy moieties, and the trifluoromethyl groups seem to exclude from such interactions and to become a wall of subnano tunnels.

The ''cisoid'' double head trifluorolactates have subnano tunnels between the sheets (Fig. 2), though that of **1d** seems too narrow (ca. 0.5 Å width). The tunnels run parallel to the hydrogen bonding networks; that is, the length of the tunnel is that of the needle. The other tunnels in the needle of **1f** have trapezoid tunnels with 3 Å × 3 Å, of which walls of the tunnel were covered by two trifluoromethyl groups per unit length and top and bottom is made by methylene moiety of diol linker. The tunnel in the needle of **1a** has distorted hexagonal tunnels with 4 Å × 6 Å, which walls were covered by four trifluoromethyl groups per unit length.



Scheme 4.

The importance of constructing nano tubes, channels, and tunnels hardly required restatements herein [48–52]. They have been accepting interests as reaction fields, tools for molecular recognition [51,53–55], as well as the materials for gas storage [56]. More recently, a possible usage of nano tunnels for nano pumps has been proposed [57,58]. For these purposes of usage, the porous material with dense wall is essential. Contrary to the conventional organic nano and subnano tunnels which have been constructed mainly by stacking of molecular daughnuts, rings, or nets by van der Waals interactions [51,59–63], the double head trifluorolactates knot up the dense sheet at first, then accumulation of the sheet by van der Waals interaction constructs the tunnels. Thus, they have no side holes or gaps throughout the tunnels.

4. Conclusion

In conclusion, we have developed a new supramolecular synthon for crystal engineering construction of subnano tunnels via accumulation of corrugated sheets. For the tunnel construction, ''cisoid'' conformation of the two trifluorolactic moieties toward the linker polymethylene to give a square or trapezoid wave pattern supramolecular sheet is essential. For the construction of far larger tunnel, van der Waals motif on the surface of the square wave pattern for connection of surface by surface is needed. Studies on further properties and utilization of the present porous compounds are in progress.

5. Experimental

5.1. General

Preparation of trifluorolactic acid was described in our previous report [64]. All commercially available reagents and solvents were employed without further purification.

Chromatography on silicagel was performed using a forced flow of the solvent system on Merck silica gel (Kieselgel 60, 230–400 mesh). GC analyses were performed using Shimadzu GC-12A system connected to GL-Science CP-Cyclodex-β-256M Capillary column. Melting points were obtained on Yanagimoto MP-S3 apparatus and are uncorrected.

^{1}H (200 MHz), ^{19}F (188 MHz), and ^{13}C (50.3 MHz) NMR spectra were recorded on Varian VXR-200 spectrometers. Chemical shifts are reported in δ ppm from tetramethylsilane (δ 0.0 ppm for ^{1}H and ^{13}C NMR) and C_6F_6 (δ 0.0 ppm for ^{19}F NMR). Coupling constants (J) are reported in hertz. Optical rotation was measured in a cell with 50 mm length and 1 ml capacity using a Horiba High Sensitive Polarimeter SEPA-300. Elemental analyses were performed on Perkin-Elmer series II CHNS/O Analyzer 2400. GC–MS was performed on a Hewlett Packard HP5971A.

Intensity measurements for X-ray crystallographic analyses were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo Kα radiation.

5.2. Preparation of the trifluorolactates

Preparations of trifluorolactic acid and trifluorolactates were summarized in our previous reviews [65,66]. General procedure for preparations and spectroscopic data for single head trifluorolactates **1a**, **1b** and double head trifluorolactate with hexamethylene linker **2d** had been reported [39,67,68].

5.3. Trimethylene di(trifluorolactate) *2a*

Melting point 56–57 °C. IR (KBr) 3468, 1746 cm^{-1}. ^{19}F NMR (188 MHz, $CDCl_3$) δ 85.6 (d, J = 9 Hz, 6F) ppm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (quin, J = 25 Hz, 2H), 3.48 (m, 2H), 4.37 (quin, J = 23 Hz, 2H), 4.46 (quin, J = 24 Hz, 2H), 4.50 (quar, J = 21 Hz, 2H) ppm. Element anal. calcd. for $C_9H_{10}F_6O_6$: C, 32.94; H, 3.07%. Found: C, 33.21; H, 3.36%. GC–MS m/z 329 [M + 1].

Crystallographic data for **2a**: M_w = 328.16, colorless needle, orthorhombic, space group $P2_12_12_1$ (#19), a = 16.274, b = 19.296, c = 5.260, V = 1651.8 Å^3, Z = 4, D_c = 1.320 g/cm^3, μ(Mo Kα) = 1.49 cm^{-1}, T = 296 K, $2\theta_{max}$ = 55.0°, no. of measured = 2167, no. of observations ($I > 2.00\sigma(I)$) = 1156, no. of parameters = 205, R = 0.083, R_W = 0.091, residual electron density = 0.16/−0.21 eÅ^{-3}.

5.4. Tetramethylene di(trifluorolactate) *2b*

Melting point 82–84 °C. IR (KBr) 3508, 3436, 1758, 1746 cm^{-1}. ^{19}F NMR (188 MHz, $CDCl_3$) δ 85.6 (d, J = 8 Hz, 6F) ppm. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.81 (quin, J = 11 Hz, 4H), 2.85 (s, 2H), 4.33 (m, 2H), 4.51 (t, J = 14 Hz, 4H) ppm. Element anal. calcd. for $C_{10}H_{12}F_6O_6$: C, 35.10; H, 3.53%. Found: C, 34.72; H, 3.90%. GC–MS m/z 343 [M + 1].

Crystallographic data for **2b**: M_w = 342.19, colorless needle, monoclinic, space group $P2_1$ (#4), a = 7.326, b = 5.142, c = 18.189, β = 95.921°, V = 681.6 Å^3, Z = 2, D_c = 1.667 g/cm^3, μ(Mo Kα) = 1.84 cm^{-1}, T = 292 K, $2\theta_{max}$ = 55.0°, no. of measured = 2824, no. observations ($I > 0.00\sigma(I)$) = 1482, no. of parameters = 199, R = 0.089, R_W = 0.099, residual electron density = 0.31/−0.30 eÅ^{-3}.

5.5. Pentamethylene di(trifluorolactate) *2c*

Melting point 100–102 °C. IR (KBr) 3432, 1754, 1742 cm^{-1}. ^{19}F NMR (188 MHz, $CDCl_3$) δ 85.6 (d, J = 8 Hz, 6F) ppm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (quin, J = 32 Hz, 2H), 1.74 (quin, J = 28 Hz, 4H), 2.60 (s, 2H), 4.26–4.31 (m, 2H), 4.36–4.41 (m, 2H), 4.47 (quar, J = 21 Hz, 2H) ppm. Element anal. calcd. for $C_{11}H_{14}F_6O_6$: C, 37.09; H, 3.96%. Found: C, 36.83; H, 4.19%. GC–MS m/z 357 [M + 1].

Crystallographic data for **2c**: M_w = 356.22, colorless needle, monoclinic, space group $C2$ (#5), a = 18.816, b = 5.137, c = 7.756, β = 96.202°, V = 745.3 Å^3, Z = 2, D_c = 1.587 g/cm^3, μ(Mo Kα) = 1.71 cm^{-1}, T = 292 K, $2\theta_{max}$ = 55.0°, no. of measured = 839, no. observations ($I > 1.20\sigma(I)$) = 648, no. of parameters = 111, R = 0.069, R_W = 0.056, residual electron density = 0.47/−0.51 eÅ^{-3}.

5.6. Heptamethylene di(trifluorolactate) *2e*

Melting point 92–94 °C. IR (KBr) 3448, 1750, 1740 cm^{-1}. ^{19}F NMR (188 MHz, $CDCl_3$) δ 85.6 (d, J = 6 Hz, 6F) ppm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37 (m, 6H), 1.71 (quin, J = 20 Hz, 4H), 3.41 (d, J = 8 Hz, 2H), 4.26 (t, J = 13 Hz, H), 4.28 (t, J = 13 Hz, H), 4.36 (t, J = 13 Hz, H), 4.38 (t, J = 13 Hz, H), 4.47 (quin, J = 29 Hz, 2H) ppm. Element anal. calcd. for $C_{13}H_{18}F_6O_6$: C, 40.63; H, 4.72%. Found: C, 40.79; H, 5.0%. GC–MS m/z 385 [M + 1].

Crystallographic data for **2e**: M_w = 384.24, colorless needle, monoclinic, space group $P2_1$(#4), a = 20.812, b = 5.128, c = 7.966, β = 96.279°, V = 845.0 Å^3, Z = 2, D_c = 1.510 g/cm^3, μ(Mo Kα) = 1.57 cm^{-1}, T = 296 K, $2\theta_{max}$ = 55.0°, no. of measured = 1033, no. observations ($I > 3.00\sigma(I)$) = 981, no. of parameters = 233, R = 0.048, R_W = 0.045, residual electron density = 0.75/−0.41 eÅ^{-3}.

5.7. Octamethylene di(trifluorolactate) *2f*

Melting point 70–72 °C. IR (KBr) 3452, 1750, 1734 cm^{-1}. ^{19}F NMR (188 MHz, $CDCl_3$) δ 85.6 (d, J = 8 Hz, 6F) ppm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 8H), 1.71 (quin, J = 21 Hz, 4H), 3.42 (s, 2H), 4.26 (t, J = 13 Hz, H), 4.28 (t, J = 14 Hz, H), 4.36 (t, J = 13 Hz,

H), 4.38 (t, $J = 14$ Hz, H), 4.46 (quar, $J = 20$ Hz, 2H) ppm. Element anal. calcd. for C14H20F6O6: C, 42.22; H, 5.06%. Found: C, 42.0; H, 5.29%. GC–MS m/z 385 $[M + 1]$.

Crystallographic data for **2f**: $M_w = 398.30$ colorless needle, monoclinic, space group $P2_1$(#4), $a = 8.038$, $b = 22.966$, $c = 5.151$, $b = 90.003^\circ$, $V = 950.9$ Å^3, $Z = 2$, $D_c = 1.391$ g/cm^3, μ(Mo Kα) $= 1.42$ cm^{-1}, $T = 120$ K, $2\theta_{max} = 55.0^\circ$, no. of measured $= 2066$, no. observations $(I > 1.20\sigma(I)) = 1806$, no. of parameters $= 255$, $R = 0.070$, $R_W = 0.082$, residual electron density $= 0.35/-0.43$ eÅ^{-3}.

5.8. 2,2,3,3,4,4,5,5-Octafluorohexamethylenedi(trifluorolactate) **2f**

Crystallographic data for **2g**: $M_w = 514.17$ colorless plate, monoclinic, space group $P2_1$(#4), $a = 5.156$, $b = 11.412$, $c = 14.916$, $b = 97.639^\circ$, $V = 869.81$ Å^3, $Z = 2$, $D_c = 1.963$ g/cm^3, μ(Mo Kα) $= 2.43$ cm^{-1}, $T = 296$ K, $2\theta_{max} = 55.0^\circ$, no. of measured $= 2101$, no. observations $(I > 3.020\sigma(I)) = 2015$, no. of parameters $= 321$, $R = 0.028$, $R_W = 0.030$, residual electron density $= 0.15/-0.24$ eÅ^{-3}.

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