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SYNTHESIS OF NEW HIGH PERFORMANCE LUBRICANTS AND SOLID LUBRICANTS

Progress Report

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DISCLAIMER

SYNTHESIS OF NEW HIGH PERFORMANCE LUBRICANTS AND SOLID LUBRICANTS

Technical Progress Report

We have been making very substantial progress during the first year of our Department of Energy grant number DE-FG05-91ER12119 on many fronts. We have started to make a number of classes of new perfluoropolyethers both in the solid lubricant area and liquid lubricant area.

One of the steps that we have taken that we think is most significant is that we have prepared some chlorofluoroethers for testing as additives for normal petroleum and polyalphaolefin lubricants which are so widely used in the United States. We have recently made (see pages 53 and 54 of our original proposal) arrangements with Shell Development Company located in Houston, Texas to test these as motor oil additives and polyalphaolefin additive packages. Dr. Larry Olejnik, Manager of Fuels and Lubricants at Shell Development company's Westhollow Research Center in Houston is in charge of this testing. We are very anxious in the future to receive reports that confirm our feelings that these have the potential to become superb energy saving additives. As stated in the proposal, these perfluoropolyethers are not soluble in hydrocarbons. On the other hand, these chlorofluoropolyethers are soluble in substantial amounts in simple hydrocarbons. These are uniquely capable of being additives that flow with the motor oil or the polyalphaolefin. Teflon (polytetrafluoroethylene) which has been used as an additive in motor oils is not soluble in hydrocarbons and is simply burnished (coated) on piston and cylinder walls. In spite of the fact that fluorocarbons are extraordinarily stable, no oil or fluorocarbon is stable for long periods of time at the temperatures at which internal combustion engines

operate. With a flow through system, such as would be possible with the chlorofluoro soluble additives, no decomposition of the fluorocarbon is expected in motor oils.

We have also launched a major effort toward the synthesis of spherical perfluoropolyethers. The idea here is that this novel class of perfluoropolyethers may work as "molecular ball bearings" to produce materials with extremely unusual lubricating properties. Very shortly some of these will be tested by Dr. Bill Jones of the Tribology Laboratories at the NASA Lewis Research Center in Cleveland. You will note that we have prepared and characterized a wide range of materials.

Perfluoro(Pentaerythrityl tetraoctyl ether)

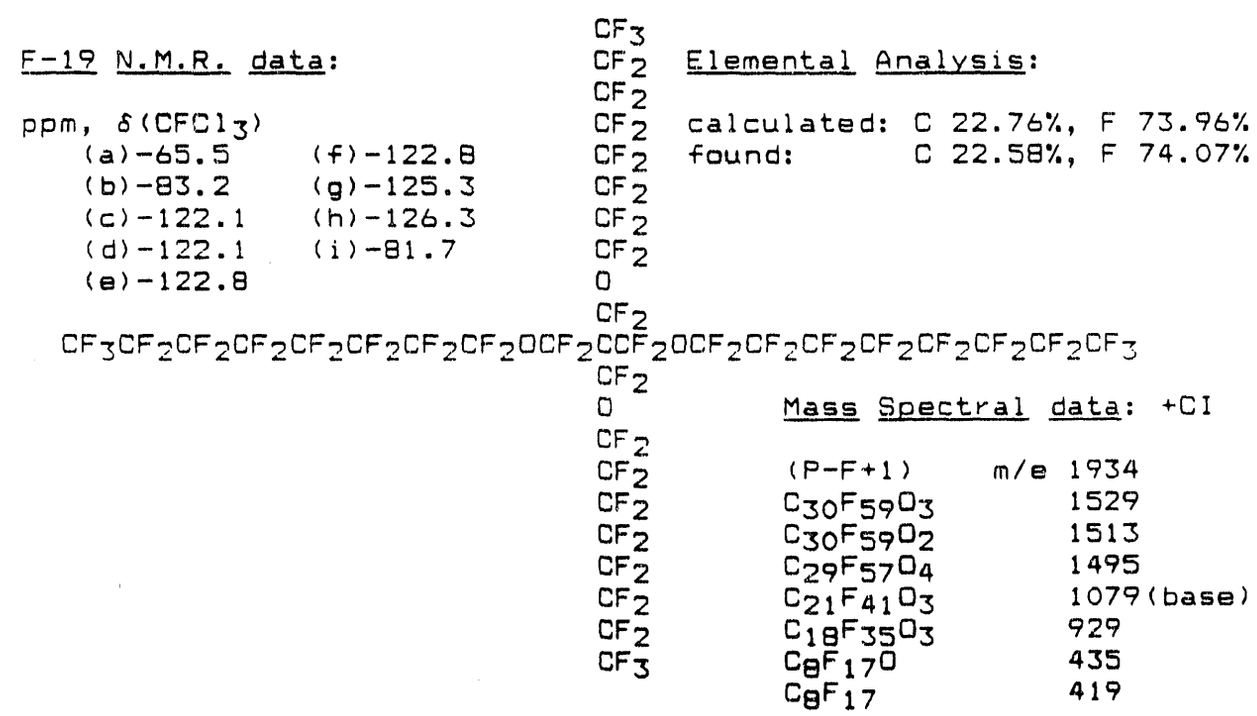
$C(-CH_2-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3)_4 \xrightarrow{F_2}$ 19% yield

M.W. 1952 $C(-\underset{a}{CF_2}-O-\underset{b}{CF_2}-\underset{c}{CF_2}-\underset{d}{CF_2}-\underset{e}{CF_2}-\underset{f}{CF_2}-\underset{g}{CF_2}-\underset{h}{CF_2}-\underset{i}{CF_3})_4$

F-19 N.M.R. data:

ppm, $\delta(CFCl_3)$

(a) -65.5	(f) -122.8
(b) -83.2	(g) -125.3
(c) -122.1	(h) -126.3
(d) -122.1	(i) -81.7
(e) -122.8	



Elemental Analysis:

calculated: C 22.76%, F 73.96%
found: C 22.58%, F 74.07%

Mass Spectral data: +CI

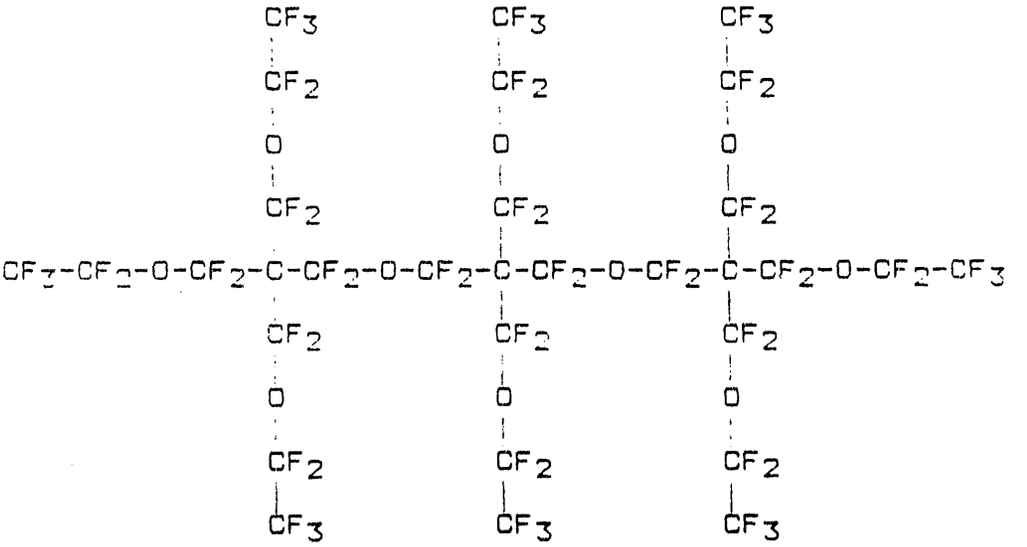
(P-F+1)	m/e 1934
$C_{30}F_{59}O_3$	1529
$C_{30}F_{59}O_2$	1513
$C_{29}F_{57}O_4$	1495
$C_{21}F_{41}O_3$	1079 (base)
$C_{18}F_{35}O_3$	929
$C_8F_{17}O$	435
C_8F_{17}	419

Perfluoro(Tripentaerythrityl octaethyl ether)

$$[(CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-})_3C\text{-}CH_2\text{-}O\text{-}CH_2\text{-}]_2C[\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3]_2 \xrightarrow[19\%\ \text{yield}]{F_2}$$

M.W. 1748 $[(CF_3\text{-}CF_2\text{-}O\text{-}CF_2\text{-})_3C\text{-}CF_2\text{-}O\text{-}CF_2\text{-}]_2C[\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF_3]_2$

(a) (b) (c) (d) (d) (c) (b) (a)



F-19 N.M.R. data: ppm, $\delta(CFCl_3)$

(a)-87.7
(b)-89.0
(c)-66.3
(d)-65.3

Elemental Analysis:

calculated: C 21.30%, F 69.55%
found: C 21.05%, F 69.31%

Mass Spectral data: +CI

(P-F+1)	m/e 1730
$C_{20}F_{39}O_7+1$	1094
$C_{17}F_{35}O_5$	949
$C_{11}F_{23}O_4$	633
$C_{11}F_{23}O_3$	617 (base peak)
$C_{10}F_{21}O_3$	567
$C_9F_{17}O_3$	479
$C_8F_{17}O_2$	451
$C_7F_{13}O_2$	363
C_3F_7O	185
C_2F_5	119

Perfluoro(Pentaerythrityl tetraheptyl ether)

$C(-CH_2-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3)_4 \xrightarrow[9\%\ yield]{F_2}$

M.W. 1752

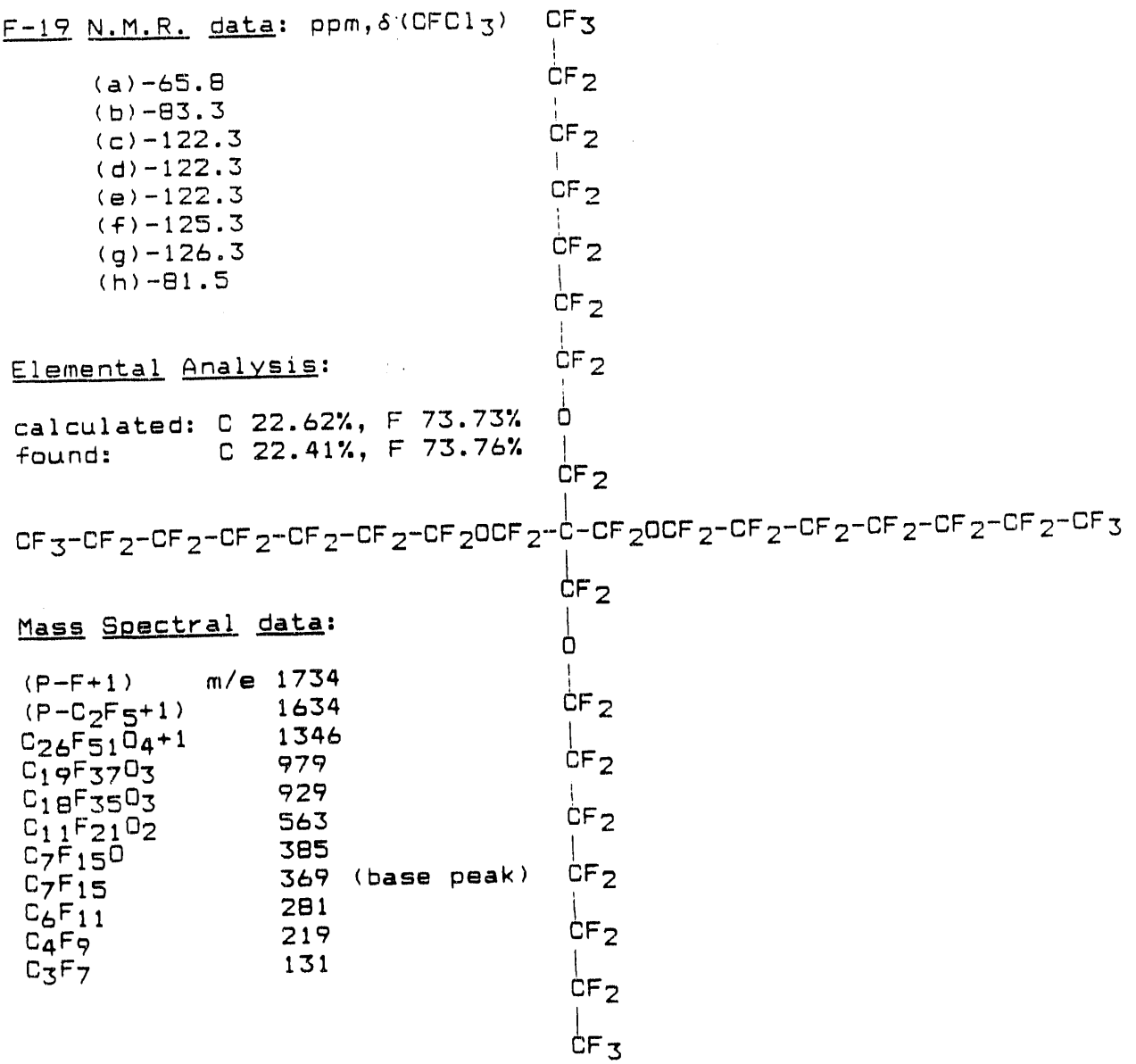
$$C(-\underset{a}{CF_2}-O-\underset{b}{CF_2}-\underset{c}{CF_2}-\underset{d}{CF_2}-\underset{e}{CF_2}-\underset{f}{CF_2}-\underset{g}{CF_2}-\underset{h}{CF_3})_4$$

F-19 N.M.R. data: ppm, δ ($CFCl_3$)

(a) -65.8
(b) -83.3
(c) -122.3
(d) -122.3
(e) -122.3
(f) -125.3
(g) -126.3
(h) -81.5

Elemental Analysis:

calculated: C 22.62%, F 73.73%
found: C 22.41%, F 73.76%



Mass Spectral data:

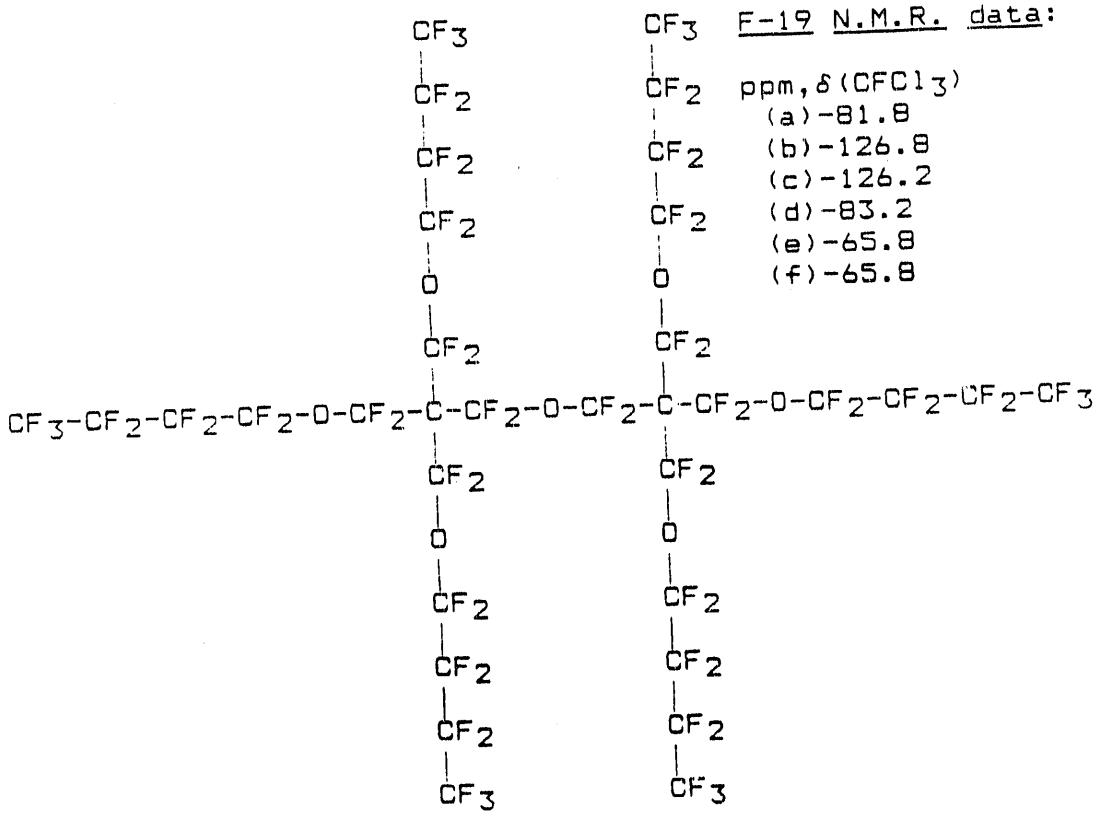
(P-F+1)	m/e 1734	
(P-C_2F_5+1)	1634	
$C_{26}F_{51}O_4$+1	1346	
$C_{19}F_{37}O_3$	979	
$C_{18}F_{35}O_3$	929	
$C_{11}F_{21}O_2$	563	
$C_7F_{15}O$	385	
C_7F_{15}	369	(base peak)
C_6F_{11}	281	
C_4F_9	219	
C_3F_7	131	

Perfluoro(Dipentaerythrityl hexabutyl ether)

$[(CH_3-CH_2-CH_2-CH_2-O-CH_2-)_3C-CH_2-]_2O \xrightarrow[20\%\ yield]{F_2}$

M.W. 1850

$[(\underset{a}{CF_3}-\underset{b}{CF_2}-\underset{c}{CF_2}-\underset{d}{CF_2}-O-\underset{e}{CF_2}-)_3C-\underset{f}{CF_2}-]_2O$



F-19 N.M.R. data:

ppm, $\delta(CFCl_3)$

(a) -81.8
(b) -126.8
(c) -126.2
(d) -83.2
(e) -65.8
(f) -65.8

Elemental Analysis:

calculated:	C 22.07%,	F 71.88%
found:	C 21.66%,	F 71.60%

Mass Spectral data:

	m/e	
(P-F)	1831	
$(P-C_3F_7)$	1681	
$C_{30}F_{59}O_7$	1593	
$C_{26}F_{51}O_6$	1377	
$C_{22}F_{41}O_6$	1139	
$C_{17}F_{35}O_4$	933	
$C_{17}F_{35}O_3$	917	(base peak)
$C_{13}F_{25}O_4$	695	
$C_{13}F_{25}O_3$	679	
$C_9F_{15}O_3$	441	
$C_8F_{15}O$	397	
$C_5F_{11}O$	285	
C_4F_9O	235	
C_4F_9	219	
C_3F_7	169	

Perfluoro(Pentaerythrityl tetrahexyl ether)

$C(-CH_2-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3)_4 \xrightarrow{F_2}$ 29% yield $C(-CF_2-O-CF_2-CF_2-CF_2-CF_2-CF_2-CF_3)_4$

M.W. 1552

a b c d e f g

F-19 N.M.R. data: ppm, $\delta(CFCl_3)$

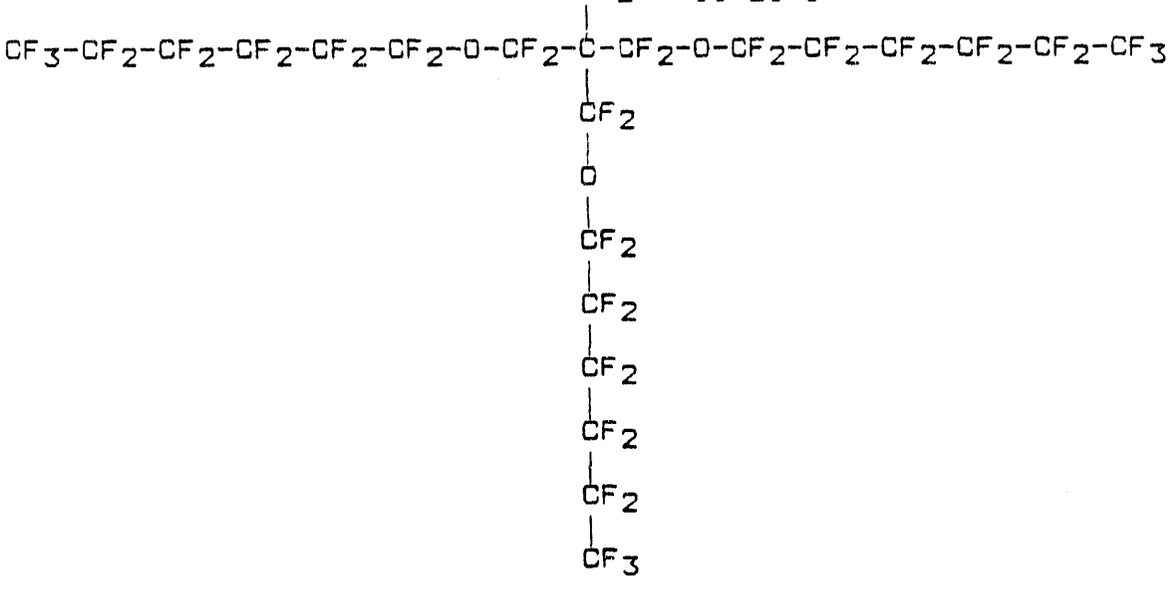
(a)-65.3
(b)-83.0
(c)-122.3
(d)-122.8
(e)-125.0
(f)-126.3
(g)-81.5

Elemental Analysis:

calculated: C 22.44%, F 73.44%
found: C 22.00%, F 73.48%

Mass Spectral data:

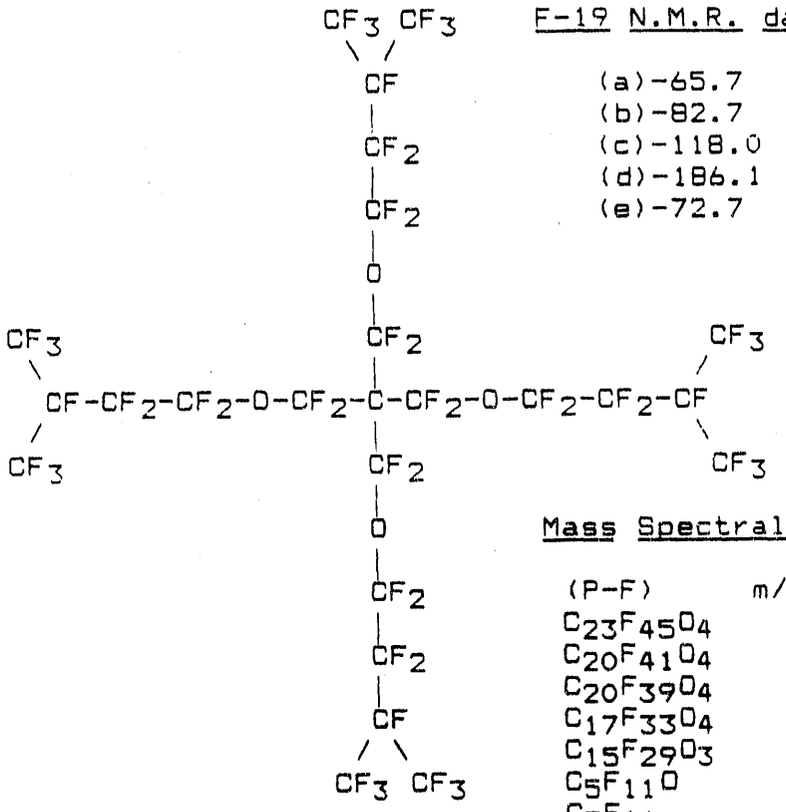
(P-F)	m/e	1533
$C_{29}F_{57}O_4$		1495
$(P-C_4F_9)$		1333
$(P-C_6F_{13}+1)$		1234
$C_{23}F_{45}O_4$		1195
$C_{20}F_{39}O_4$		1045
$C_{19}F_{37}O_4$		995
$C_{18}F_{35}O_4$		945
$C_{17}F_{33}O_4$		895
$C_{17}F_{33}O_3$		879 (base peak)
$C_{16}F_{31}O_3$		829
$C_{16}F_{31}O_2$		813
$C_{11}F_{21}O_3$		579



Perfluoro(Pentaerythrityl tetraisopentyl ether)

$$C(-CH_2-O-CH_2-CH_2-CH[-CH_3]_2)_4 \xrightarrow{F_2} C(-CF_2-O-CF_2-CF_2-CF[-CF_3]_2)_4$$

M.W. 1352 — 19% yield — a b c d e



F-19 N.M.R. data: ppm, $\delta(CFCl_3)$

(a) -65.7
(b) -82.7
(c) -118.0
(d) -186.1
(e) -72.7

Mass Spectral data:

(P-F)	m/e 1333	
$C_{23}F_{45}O_4$	1195	
$C_{20}F_{41}O_4$	1083	
$C_{20}F_{39}O_4$	1045	(base peak)
$C_{17}F_{33}O_4$	895	
$C_{15}F_{29}O_3$	779	
$C_5F_{11}O$	285	
C_5F_{11}	269	
C_5F_9O	247	
C_4F_7	181	

Elemental Analysis:

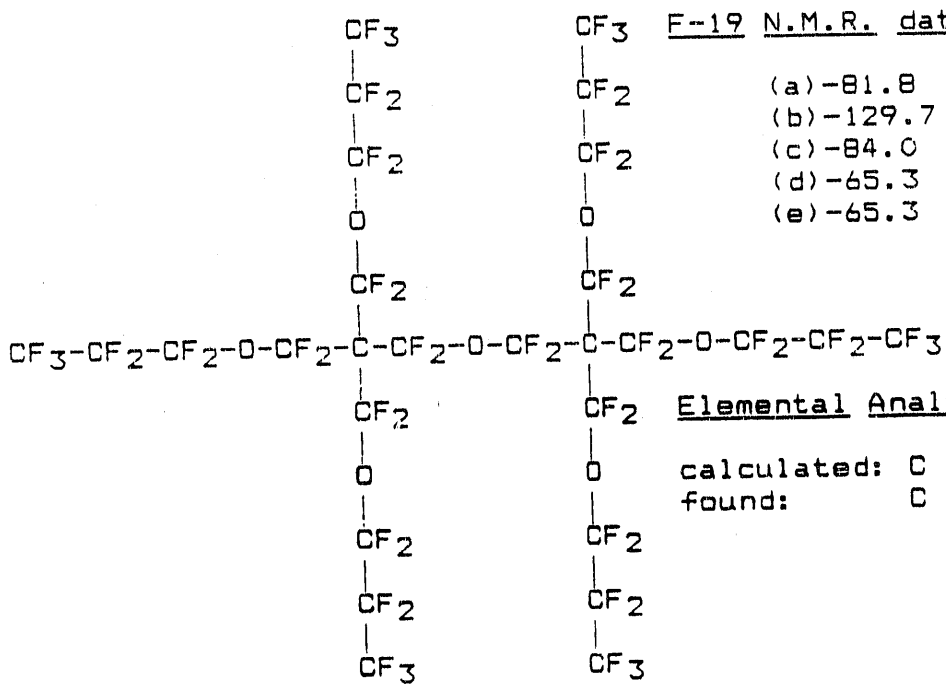
calculated: C 22.21%, F 73.06%
found: C 21.78%, F 73.04%

Perfluoro(Dipentaerythrityl hexapropyl ether)

$[(CH_3-CH_2-CH_2-O-CH_2-)_3C-CH_2-]_2O \xrightarrow[30\%\ yield]{F_2}$

$[(\underset{a}{CF_3}-\underset{b}{CF_2}-\underset{c}{CF_2}-O-\underset{d}{CF_2}-)_3C-\underset{e}{CF_2}-]_2O$

M.W. 1550



F-19 N.M.R. data: ppm, $\delta(CFCl_3)$

(a) -81.8
(b) -129.7
(c) -84.0
(d) -65.3
(e) -65.3

Elemental Analysis:

calculated: C 21.69%, F 71.08%
found: C 21.38%, F 70.81%

Mass Spectral data: +CI

	m/e
(P-F+1)	1532
$C_{25}F_{49}O_7+1$	1344
$(P-C_4F_9O+1)$	1316
$C_{14}F_{29}O_4$	783
$C_{14}F_{29}O_3$	767 (base peak)
$C_{12}F_{25}O_3$	667
$C_{11}F_{21}O_3$	579
$C_{10}F_{21}O_2$	551
$C_7F_{13}O_2$	363
C_4F_9O	235
C_3F_7O	185
C_3F_7	169
C_2F_4	100

Perfluoro(Pentaerythrityl tetrapentyl ether)

$$C(-CH_2-O-CH_2-CH_2-CH_2-CH_2-CH_3)_4 \xrightarrow{F_2} C(-\underset{a}{CF_2}-O-\underset{b}{CF_2}-\underset{c}{CF_2}-\underset{d}{CF_2}-\underset{e}{CF_2}-\underset{f}{CF_3})_4$$

41% yield

M.W. 1352

F-19 N.M.R. data: ppm, $\delta(CFCl_3)$

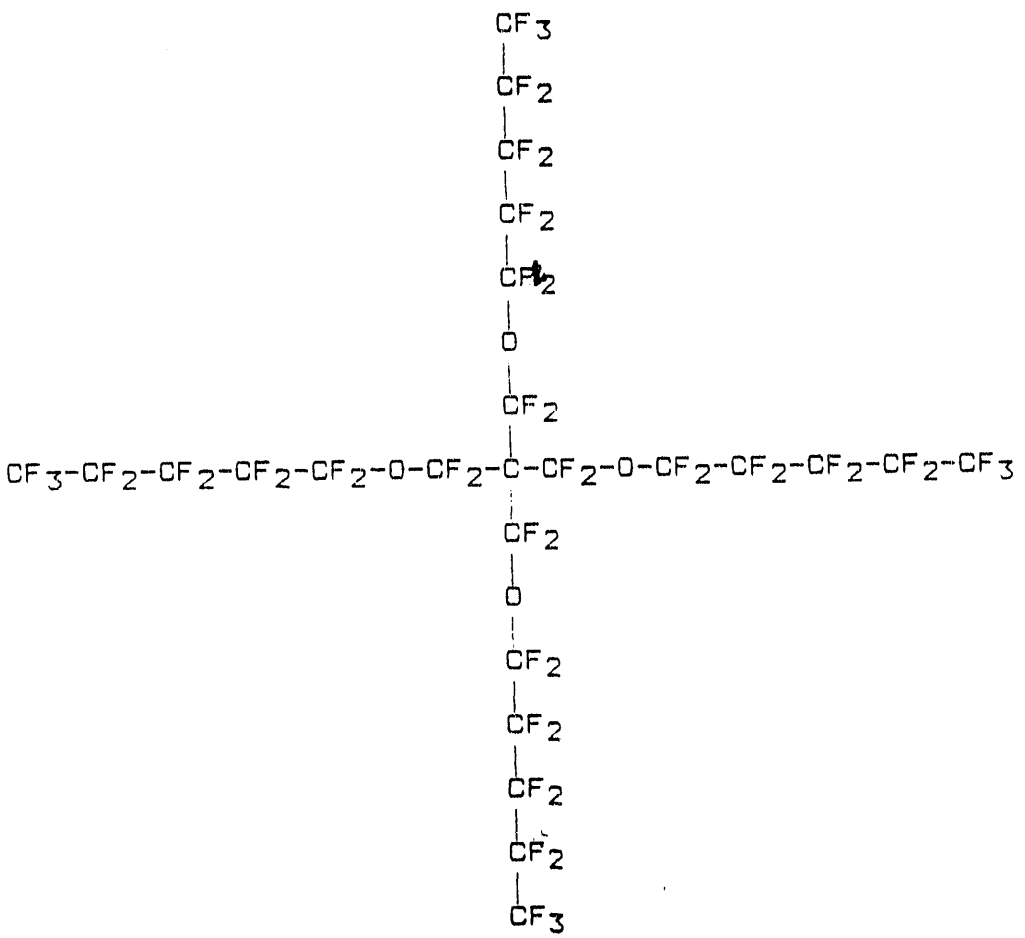
(a) -65.5
(b) -83.0
(c) -123.0
(d) -125.3
(e) -126.3
(f) -81.4

Mass Spectral data: (+CI)

(P-F+1)	m/e	1334 (base)
$(P-C_2F_5)$		1233
$(P-C_3F_7)$		1183
$(P-C_5F_{11}O+1)$		1068
$C_{20}F_{39}O_4+1$		1046
$C_{15}F_{29}O_3$		779
$C_{12}F_{23}O_3$		629
$C_{10}F_{17}O_3$		491
C_5F_{11}		269
C_4F_7		181
C_3F_5		131

Elemental Analysis:

calculated: C 22.21%, F 73.06%
found: C 21.86%, F 73.35%



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