

donor to compete with water and chlorine for coordination positions of cobalt. This is in line with the low stability of the blue cobalt chloride acetate, which decomposes above 19.5°C. even under acetone (2). In the system cobalt chloride-*tert*-butanol-water, $\text{CoCl}_2 \cdot 4\text{H}_2\text{O} \cdot 2\text{BuOH}$ was found in addition to the hexa-, di-, and monohydrate and an alcoholate (12). However, the mixed solvate was in equilibrium with only a narrow range of liquid compositions, showing the alcohol to be a comparatively weak ligand. The absence of lower hydrates in the present system and the wide range of compositions over which the mixed solvate prevailed was probably due to the strong electron donor properties of dioxane together with its bidentate nature.

The color of solutions in the nickel chloride system was emerald green, acquiring a yellowish tinge only at very high dioxane contents. The former color is indicative of paramagnetic nickel, either hexacoordinate octahedral or tetra-coordinate tetrahedral (17). At high water contents, the prevalent form was $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$. With increasing dioxane content, either some water was replaced by dioxane while maintaining the ionic nature of the complex, or chlorine became a covalent ligand owing to the lower dielectric constant of the medium. The solid diaquomonodioxanate could be the octahedral $[\text{NiCl}_2(\text{H}_2\text{O})_2(\text{C}_4\text{H}_8\text{O}_2)]$, matching the probable structure of the corresponding cobalt complex. The less likely tetrahedral structure $[\text{Ni}(\text{H}_2\text{O})_2(\text{C}_4\text{H}_8\text{O}_2)]\text{Cl}_2$ has the advantage that it might account for the hydrolysis during desolvation of the nickel solvate. The brownish yellow color of solid nickel chloride monodioxanate and the yellowish tint of solutions of very high dioxane content are indicative of a square planar and diamagnetic complex (17).

CONCLUSIONS

The two diagrams were qualitatively and quantitatively similar. The hexahydrates of the two chlorides were the solids in equilibrium with solutions rich in water. Because of their hygroscopicity, the two solid monodioxanates only coexisted with solutions of such high dioxane content that they contained little dissolved salt. The two diaquomonodioxanates were the solid phases prevailing over most of the diagram where solid and liquid phases coexisted, including the region where there were two immiscible liquids. This region expanded with increasing temperature. According to their color, the light, dioxane-rich phase contained tetra-

covalent complexes of both metals and the heavy layer hexacoordinate cobalt and also probably hexacoordinate nickel.

The exothermic reaction between the anhydrous chlorides and dioxane, the thermal stability and low vapor pressure of the diaquomonodioxanates and monodioxanates, and the release of water before that of dioxane during the progressive desolvation of the diaquomonodioxanates all indicate that dioxane is a rather strong ligand. The bidentate nature of dioxane is demonstrated by the foregoing as well as by the relation between the composition of its complexes, their color, and the coordination chemistry of bivalent cobalt and nickel.

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Fluoroalkyl Phosphonitrilates, a New Class of Potential Fire-Resistant Hydraulic Fluids and Lubricants

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The synthesis of various trimeric and tetrameric aryl-1,1-di-*H*-polyfluoroalkyl phosphonitrilates (III), a new class of compounds, is reported. The effects of structural modifications on properties such as density, viscosity, ASTM slope, pour point, and spontaneous ignition temperature are discussed.

TRIMERIC and tetrameric polyfluoroalkyl phosphonitrilates (Ia, Ib) as well as aryl-1,1,ω-tri-*H*-polyfluoroalkyl phosphonitrilates (IIa, IIb) (5, 6, 8, 9, 10) have recently been evaluated for potential use as fire-resistant naval hydraulic fluids (5, 6).

Representatives of I and II meet many requirements specified for certain lubricants and hydraulic fluids (3, 4, 7),

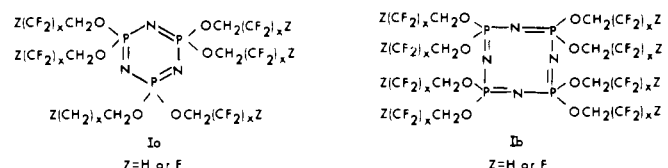
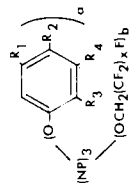
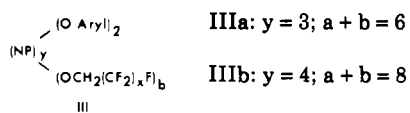
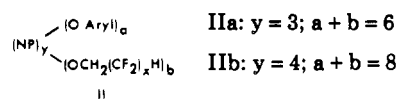


Table I. Trimeric (Aryl-1,1-di-*H*-polyfluoroalkyl) Phosphonitrilates

Run No.	Frac- tion No.	Materials Charged				Yield, %	Boiling Point, °C./Mm.	Refractive Index, n _D ²⁰	Density, G./Ml.	Kinematic Viscosity, cs.		ASTM Slope	Pour Point, °F.	Spontaneous Ignition Temp., °F. ^a	Aryloxy Content ^a	% Nitrogen	
		R ₁	R ₂	R ₃	R ₄					100° F.	210° F.					Calcd.	Found
1	3	H	H	H	H	11.8	121-140/0.02-0.03	1.3950	1.54	13.3	2.37	0.97	-15	1175	0.87	5.75	5.81
2	3	H	H	H	H	48.0	140-173/0.02	1.4321	1.46	23.4	4.00	0.91	-10	1175	1.68	5.85	6.02, 5.77
3	2 ^b	H	H	H	H	17.8	173-198/0.02	1.4825	1.41	49.8	5.45	0.86	+5	1225	3.22	5.92	5.86, 5.99
4	2 ^b	H	H	H	H	22.8	160-190/0.03-0.05	1.4369	1.39	28.9	3.45	0.97	+20	1200	3.82	5.96	6.04, 6.06
5	3	H	H	H	H	41.6	190-254/0.02-0.03	1.5051	1.59	79.3	6.75	0.87	+20	1225	5.22	6.02	6.11, 6.11
6	3	H	H	H	H	17.1	254-286/0.03-0.09	1.5681	1.49	315.3	14.8	0.82	-10	1125	2.00	3.76	3.70, 3.80
7	3	H	H	H	H	15.0	160-182/0.03	1.3902	1.49	45.5	4.80	0.90	+5	1175	3.27	4.28	4.49, 4.32
8	3	H	H	H	H	17.3	182-221/0.02-0.05	1.4433	1.49	79.4	6.45	0.88	+35	1175	3.27	4.28	4.49, 4.32
9	3	H	H	H	H	11.6	221-267/0.05-0.7	1.5039	1.41	166.9	9.39	0.90	+15	1025	2.76	2.49	2.33, 2.35
10	3	H	H	H	H	57.1	190-230/0.1-0.3	1.3702	1.71	177.4	9.77	0.88	+15	1050	1.94	5.65	5.37, 5.49
11	3	H	H	H	H	8.3	230-240/0.1-0.4	1.3820	1.70	30.4	3.61	0.96	-5	1175	2.38	5.62	5.71, 5.54
12	3	H	H	H	H	17.4	240-252/0.4-0.8	1.4189	1.61	43.0	4.42	0.93	+20	1225	3.46	5.54	5.75, 5.61
13	3	CH ₃	H	H	H	20.6	156-186/0.2	1.4320	1.45	53.3	4.76	0.96	-10	1200	2.09	4.60	4.46
14	3	CH ₃	H	H	H	32.8	186-207/0.2	1.4523	1.42	75.8	5.99	0.91	-10	1250	3.00	4.60	4.46
15	3	CH ₃	H	H	H	19.6	207-247/0.2	1.4956	1.36	82.7	7.26	0.83	+5	1275	3.00	4.60	4.46
16	3	CH ₃	H	H	H	42.8	161-182/0.05-0.07	1.4152	1.49	238.9	11.55	0.86	+35	1275	4.00	4.60	4.46
17	3	CH ₃	H	H	H	23.2	161-232/0.05-0.09	1.4375	1.44	51.1	4.90	0.93	+40	1200	1.78	3.60	3.37, 3.45
18	3	CH ₃	H	H	H	18.5	232-262/0.09-0.9	1.4980	1.32	88.4	6.75	0.89	0	1175	2.81	3.92	2.86, 3.83
19	3	CH ₃	H	H	H	11.8	168-180/0.05-0.06	1.3881	1.53	187.0	10.85	0.84	+15	1175	3.68	4.24	4.10, 4.13
20	3	CH ₃	H	H	H	40.0	180-230/0.06-0.09	1.4292	1.48	359.0	10.52	0.97	+40	1200	3.18	5.04	5.14
21	3	CH ₃	H	H	H	11.9	230-250/0.09-2.4	1.4870	1.39	712.1	14.10	0.98	+50	1200	4.36	5.09	4.50, 4.50
22	3	CH ₃	H	H	H	8.6	204-275/0.09-0.7	1.4891	1.30	61.2	5.14	0.93	+5	1075	3.04	5.28	5.16, 5.27
23	3	CH ₃	H	H	H	8.7	275-288/0.7-3.2	1.5199	1.25	353.3	11.38	0.93	+40	1200	3.04	5.28	5.16, 5.27
24	3	CH ₃	H	H	H	9.4	155-181/0.04-0.07	1.4374	1.41	4735.0	33.35	0.96	+70	1250	3.97	5.14	5.15, 4.99
25	3	CH ₃	H	H	H	15.8	181-251/0.07-0.1	1.4833	1.29	816.0	17.0	0.92	+60	1275	4.85	5.02	4.72, 4.75
26	3	CH ₃	H	H	H	13.1	251-296/0.1-3.0	1.5331	1.21	2058.3	27.7	0.90	+70	1275	4.85	5.02	5.39, 5.44
27	3	CH ₃	H	H	H	22.3	208-283/0.08-0.3	1.5074	1.25	53.4	4.28	1.00	+15	1100	1.56	5.50	5.30, 5.29
28	3	CH ₃	H	H	H	11.1	283-292/0.3-1.3	1.5388	1.20	542.1	13.27	0.94	+55	1100	1.20	5.29	5.50
29	3	CH ₃	H	H	H	14.4	147-182/0.05-0.07	1.4281	1.42	59.0	4.82	0.83	+5	1100	2.92	5.29	5.50
30	3	H	H	H	H	31.0	182-262/0.07-0.3	1.4720	1.32	68.2	5.90	0.97	+5	1075	2.92	5.29	5.50
31	3	H	H	H	H	17.8	142-172/0.02-0.03	1.4097	1.48	1158.5	15.00	1.03	+70	1100	1.39	5.25	5.24, 5.21
32	3	H	H	H	H	14.2	172-209/0.03-0.06	1.4451	1.38	30.6	4.03	0.89	+5	1000	2.51	4.91	4.81, 4.75
33	3	H	H	H	H	36.0	172-265/0.03-1.3	1.4773	1.33	54.8	5.86	0.84	+5	1000	2.25	5.37	5.49, 5.47
34	3	H	H	H	H	21.8	209-265/0.06-1.3	1.4977	1.28	70.3	6.96	0.83	+5	1075	4.36	5.04	5.13, 5.07
35	3	H	H	H	H	7.3	156-192/0.05-0.08	1.4211	1.41	59.0	4.82	0.83	+5	1100	2.92	5.29	5.50
36	3	H	H	H	H	14.0	192-250/0.08-3.0	1.4640	1.27	68.2	5.90	0.97	+5	1050	1.39	5.25	5.24, 5.21
37	3	H	H	H	H	21.4	187-217/0.05	1.4511	1.47	1158.5	15.00	1.03	+70	1100	1.39	5.25	5.24, 5.21
38	3	H	H	H	H	18.0	229-250/0.05-0.07	1.4937	1.42	204.6	10.95	0.85	+30	1000	2.40	5.18	5.33, 5.32
39	3	H	H	H	H	11.3	250-297/0.07-0.1	1.5281	1.36	570.3	19.20	0.83	+5	1075	4.36	5.04	5.13, 5.07
40	3	H	H	H	H	24.5	180-232/0.03	1.4330	1.49	34.8	4.32	0.88	-5	1125	1.56	4.87	4.87, 4.87
41	3	H	H	H	H	44.0	180-245/0.03-0.07	1.4593	1.46	64.2	6.00	0.87	+5	1125	1.56	4.87	4.87, 4.87
42	3	H	H	H	H	19.9	232-245/0.03-0.07	1.4941	1.41	140.1	8.80	0.87	+30	1150	1.00	5.16	5.24, 5.25
43	3	H	H	H	H	20.0	188-243/0.03-0.07	1.4327	1.50	35.7	4.37	0.89	-5	1125	1.00	5.16	5.24, 5.25

3 ^b	H	OC ₂ H ₅	H	H	1	18.4	243-274/0.07-0.4	1.4911	1.43	172.9	9.90	0.86	+30	1125	2.08	4.59	4.83, 4.76
4 ^b	H	OC ₂ H ₅	H	H	1	12.2	274-325/0.4-1.0	1.5335	1.37	483.2	16.60	0.85	+55	1150	3.22	4.14	3.80, 3.82
17	2	CH ₃ -C(=O)-	H	H	1	8.0	162-167/0.02-0.07	1.4115	1.52	44.9	4.79	0.89	°	1075	0.91	5.51	5.05
18	2	F	H	H	1	39.0	170-203/0.03-0.04	1.4468	1.52	29.7	4.08	0.87	-15	1225	2.49	5.54	5.46, 5.37
	2+3	F	H	H	1	59.3	170-241/0.03-0.07	1.4622	1.49	36.8	4.60	0.86	-10	1225	2.97	5.49	5.51, 5.55
19	3	F	H	H	1	20.1	203-241/0.03-0.07	1.4931	1.46	57.4	6.15	0.82	0	1275	3.86	5.42	5.19, 5.22
20	2	H	F	H	1	33.0	180-230/0.02-0.04	1.4561	1.53	47.4	5.15	0.87	0	1225	2.81	5.50	5.58, 5.55
	2	Cl	H	H	1	27.2	180-221/0.02-0.03	1.4642	1.52	35.6	4.57	0.84	-10	1200	2.34	5.29	5.38, 5.32
	2+3	Cl	H	H	1	51.4	180-262/0.02-0.09	1.4909	1.49	56.4	6.12	0.83	+15	1275	2.89	5.19	5.14, 5.13
21	3	Cl	H	H	1	24.2	221-282/0.03-0.09	1.5202	1.48	98.2	8.20	0.82	+5	1300	3.46	5.09	4.78, 4.83
	2	Cl	H	H	1	12.6	169-185/0.05-0.06	1.4137	1.55	36.7	4.46	0.88	-30	1200	2.68	4.39	4.46, 4.64
	2+3	Cl	H	H	2	46.5	169-232/0.06-0.08	1.4495	1.50	56.3	5.89	0.84	-20	1250	3.27	4.47	4.65, 4.74
22	3	Cl	H	H	2	33.9	185-232/0.06-0.08	1.4606	1.50	61.8	6.38	0.83	-5	1250	3.49	4.47	4.65, 4.74
	2	H	Cl	H	1	9.7	171-190/0.05	1.4489	1.55	37.1	4.53	0.87	-10	1200	2.70	5.22	5.20, 5.24
	3	H	Cl	H	1	36.5	190-234/0.05-0.06	1.4820	1.51	72.7	6.29	0.87	+10	1225	2.70	5.22	5.20, 5.24
23	2	H	H	Cl	1	16.8	145-180/0.03-0.05	1.4642	1.55	33.2	4.10	0.90	-10	1100	1.65	5.41	5.55, 5.64
	3 ^b	H	H	Cl	1	30.3	180-238/0.03-0.05	1.5202	1.51	134.4	8.20	0.90	+35	1150	2.79	5.20	5.36, 5.35
	4	H	H	Cl	1	13.2	238-273/0.07-0.4	1.5481	1.48	1019.5	19.5	0.93	+65	1250	4.25	4.95	5.12, 5.14
24	2 ^d	CH ₃	Cl	H	1	30.6	182-242/0.03-0.05	1.4749	1.48	111.3	7.20	0.92	+25	1225	2.34	5.07	5.10, 5.13
	3	CH ₃	Cl	H	1	11.4	242-273/0.05-0.09	1.5151	1.44	494.0	13.50	0.94	+55	1300	3.84	4.81	4.78, 4.83
25	2	CF ₃	Cl	H	1	11.6	273-292/0.09-2.9	1.5320	1.40	555.0	14.05	0.94	+60	1300	3.84	4.81	4.78, 4.83
	3	CF ₃	H	H	1	21.0	150-180/0.03	1.4150	1.55	26.6	3.75	0.89	-15	1175	2.00	4.92	5.01, 5.02
	4	CF ₃	H	H	1	43.7	180-215/0.03-0.05	1.4470	1.53	65.4	6.00	0.88	+5	1200	3.47	4.45	4.57, 4.54
	3	CF ₃	H	H	1	6.6	215-230/0.05-0.07	1.4711	1.52	186.9	9.70	0.89	°	1275	4.84	4.08	4.14, 4.03

^a Not ASTM procedure. See experimental section. ^b After standing for several months, this fraction was partly solid. ^c After standing for several months, this fraction contained a small amount of solids. ^d After standing for several months, this fraction solidified. ^e Not determined.



but viscosities (for Z = H) and densities of compounds of type I are high and the autogenous ignition temperatures do not exceed 1050° F. (6). Properties of compounds to type II are more attractive, but viscosities are still excessively high (6). It was, therefore, the principal objective of our investigations to lower the viscosities of compounds of type II to 43 to 50 cs. at 100° F. and 4.8 cs. or less at 210° F. by chemical modifications. It was anticipated that the replacement of the 1,1,ω-tri-*H*-polyfluoroalkoxy groups in compounds II by short-chain 1,1-di-*H*-polyfluoroalkoxy groups would reduce the degree of hydrogen bonding and, thus, afford products (type III) of lower viscosities. The use of

short-chain polyfluoro alcohols was also expected to provide for lower densities.

EXPERIMENTAL

Typical Synthesis Procedure. REACTION OF TRIMERIC PHOSPHONITRILIC CHLORIDE WITH *m*-FLUOROPHENOL AND TRIFLUOROETHANOL. A 5-liter 3-necked flask, equipped with stirrer, Dean-Stark distilling receiver, condenser, and drying tube, was charged with 36.0 grams (1.50 moles) of sodium hydride and 250 ml. of dry ether. A solution of 150.0 grams (1.50 moles) of trifluoroethanol in 150 ml. of dry ether was added dropwise to the vigorously stirred solution at such a rate that gentle spontaneous refluxing resulted. Xylene (1000 ml.) was then added and the ether was stripped to a pot temperature of 115° C. (Caution: The fluoroalkoxy compound should never be permitted to become dry or over-heated). This product was cooled to about 60° C. and 93.4 grams (1.42 moles) of potassium hydroxide (85% assay) and 168.0 grams (1.50 moles) of *m*-fluorophenol were added in small portions. After the exothermic reaction had ceased, 139.0 grams (0.40 mole) of phosphonitrilic chloride trimer, dissolved in 400 ml. of xylene, was added to the vigorously stirred and gently heated solution. Eventually, a total of 39 ml. of water was removed via the Dean-Stark receiver. Refluxing and stirring were continued for at least 16 hours thereafter. The cooled product was extracted with a 10% aqueous potassium hydroxide solution, and then washed with water. Sodium sulfate was used to break the emulsion formed in the last step. The solvent was removed by distillation under normal pressure. When the bottoms had reached 170° C., heating up to 190° C. was continued under a vacuum of 10 to 15 mm. of Hg. Finally, the reaction product was kept overnight in a bath of 150° C. at < 0.1 mm. of Hg. The reaction product was filtered and distilled in vacuo (preferably less than 0.1 mm. of Hg) over a Vigreux column wrapped with a heating tape. The end of the distillation was indicated when the pressure increased significantly or when heavy fumes were formed. Over-all yields, physical properties, and analyses of all initially liquid fractions are given in Tables I, II, and VI.

Analysis. The reaction conditions employed in the synthesis afforded complex mixtures of aryl-1,1-di-*H*-polyfluoroalkyl phosphonitrilates. The average composition of such mixtures (ratio of *a/b* in structure III) was obtained by nuclear magnetic resonance spectroscopy. Based on these results, theoretical nitrogen values were calculated. The agreement between theoretical and experimental nitrogen values (Kjeldahl method) was generally satisfactory (Tables

I, II, and VI). Previous experience with similar compounds (5, 6, 8, 9, 10) had shown that the Kjeldahl method is the only reliable analytical procedure for the determination of nitrogen in this type of compounds.

Hydrolytic Stability. Hydrolytically stable phosphonitrilates of structure III were obtained by employing a combined excess of about 25 mole% of fluoroalcohol plus phenol, refluxing the reaction mixture for prolonged periods to effect complete substitution, extracting the distilled product with aqueous base to remove traces of acidic products, and treating the product with activated charcoal.

The base and charcoal treatments were carried out as follows:

The distilled product was refluxed and stirred for 24 hours with an equal weight of 10% aqueous potassium hydroxide. Upon cooling, the product was washed until neutral, dried in vacuo over phosphorus pentoxide, and treated twice with Darco G-60 (2% of the phosphonitrilate charged) at 60° to 80° C. for 1 hour, followed by filtration through filter aid. Products treated in this fashion passed the hydrolytic stability provisions outlined in MIL-H-19457A (ships) (7) (Table III).

Evaluations. The spontaneous ignition temperatures were determined by introducing a few drops of the phosphonitrilates into a porcelain crucible contained in an electric furnace (approximately 9.5 cm. high, 4.5 cm. in diameter, and equipped with a built-in thermocouple). The temperature was increased at a rate of approximately 5° F. per minute. The temperature at which the first flash was observed was recorded. While this procedure is not as accurate as the ASTM procedure, it is much less time-consuming and gave consistent results throughout.

The Falex wear tests (11) were performed by increasing the jaw load on the journal in hourly 100-pound increments up to a total of 800 pounds. After termination of the test, the wear, as expressed in notches "take-up," and the diameter decrease of the journal (original diameter 0.25 inch) were obtained (Table IV). Tricresyl phosphate (technical grade, 80% para-, 20% meta-isomer) was run as standard under identical conditions.

Thermal stabilities were determined by heating about 20 grams of the material in a test tube in a nitrogen atmosphere at 350° C. for 4 hours. Comparison of the physical properties determined before and after the heating period was used as a measure of thermal stability (Table V).

DISCUSSION

As anticipated, replacement of the 1,1, ω -tri-*H*-polyfluoroalkoxy groups in compounds II by 1,1-di-*H*-polyfluoroalkoxy groups resulted in products (III) of considerably lower viscosities. The physical properties of aryl-1,1-di-*H*-polyfluoroalkyl phosphonitrilates (III), however, depend also on other structural modifications such as the chain length of the di-*H*-polyfluoroalkoxy group, the ratio of aryloxy to polyfluoroalkoxy groups, and the substituents attached to the aryloxy moiety. Since the trend of the property changes, thus effected, is generally independent of the size of the phosphonitrilic ring, the trimeric (IIIa) and tetrameric (IIIb) products need not be discussed separately.

In most cases, the crude reaction products were separated in fractions of lower, medium, and higher boiling ranges. Each fraction was then evaluated individually (Tables I and II).

Variation of Polyfluoroalkyl Chain Length. Three polyfluoroalcohols—2,2,2-trifluoroethanol ($x = 1$), 2,2,3,3,3-pentafluoropropanol ($x = 2$), and 2,2,3,3,4,4,4-heptafluorobutanol ($x = 3$)—were employed to investigate the relation between physical properties of various aryl-1,1-di-*H*-polyfluoroalkyl groups. Higher homologs of trifluoroethanol were of no interest, for these caused undesired density increases of the phosphonitrilates to about 1.6.

For any constant a/b ratio (number of aryloxy groups/number of polyfluoroalkoxy groups), the densities of the trimeric and tetrameric aryl-1,1-di-*H*-polyfluoroalkyl phosphonitrilates always increase with increasing chain length x , while the pour points decrease. This simple relation between chain length x on one hand and density and pour point on the other hand does not hold true for other physical properties. For example, the viscosities of three tetrameric *m*-tolyl-1,1-di-*H*-polyfluoroalkyl phosphonitrilates ($x = 1, 2, \text{ and } 3$) increase with increasing a/b ratio, not necessarily in the order of $x = 1$ to $x = 3$ but rather depending on the a/b ratio (Figure 1). Thus, extending the alkyl chain from $x = 1$ to $x = 3$ either increases or decreases the viscosity, depending on whether the a/b ratio is smaller or larger than 3.58. Other properties which respond in a similar irregular fashion to structural modifications are the ASTM slope and the spontaneous ignition temperature.

Variation of a/b Ratio. As one proceeds from a low to a high a/b ratio at constant chain length x , the boiling points, viscosities, spontaneous ignition temperatures, pour points, and refractive indices increase, while the densities decrease. Generally, the ASTM slope improves (decreases); however, when the aryloxy groups contain a relatively large substituent—e.g., *tert*-butyl—this trend may reverse.

Modification of Aryl Group. Modifications of the aryl moieties markedly affect the physical properties of the products. Up to two aromatic hydrogens were replaced by various substituents. Products in which two aromatic hydrogens were replaced always gave unfavorably high viscosities and pour points. Thus, runs 8 to 11 (Table I), in which various dimethylphenoxy groups were incorporated into the molecule, were all poor in this respect. In contrast, the isomeric products containing one ethyl group (run 12) had satisfactory viscosities; however, the spontaneous ignition temperatures were somewhat marginal. The product of run 24, containing both *m*-methyl and *p*-chloro substituents, gave the highest spontaneous ignitions in the trimeric series, but all other properties were relatively poor.

The effect of *o*-, *m*-, and *p*-chloro substitution can be seen by comparing runs 20, 22, and 23. The best over-all prop-

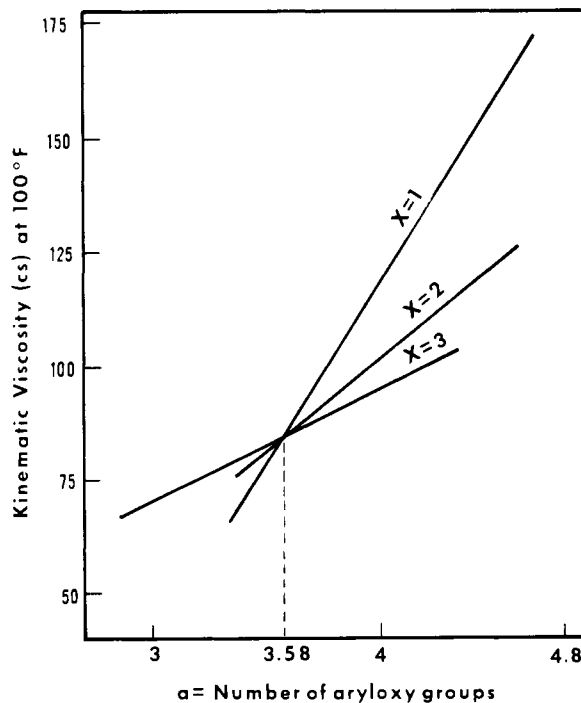
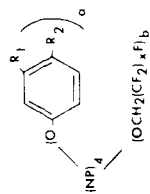


Figure 1. Kinematic viscosities at 100° F. of three tetrameric *m*-tolyl-1,1-di-*H*-polyfluoroalkyl phosphonitrilates as a function of number of aryloxy groups a

Table II. Tetrameric (Aryl-1,1-di-H-polyfluoroalkyl) Phosphonitrites



Run No.	Fraction No.	Materials Charged		Yield, %	Boiling Point, ° C./Mm.	Refractive Index, n_D^{20}	Density, G./Ml.	Kinematic Viscosity, cs.		ASTM Slope	Pour Point, ° F.	Spontaneous Ignition Temp., ° F. ^a	Aryloxy Content α	% Nitrogen	
		Phenol Type	Fluoro-alcohol type, x =					100° F.	210° F.					Calcd.	Found
26	2	H	1	18.3	160-185/0.02	1.4408	1.48	40.6	5.80	0.76	-10	1125	2.53	5.89	5.91, 5.96
	2+3	H	1	47.7	160-232/0.02	1.4656	1.44	57.0	7.26	0.73	-10	1125	3.51	5.89	5.91, 5.96
	3	H	1	29.4	185-232/0.02	1.4808	1.42	71.2	8.30	0.73	+5		4.12		
	4	H	1	13.5	232-267/0.02-0.1	1.5189	1.37	139.4	12.7	0.71	+15		5.47		
27	3 ^c	H	2	36.3	200-245/0.06-0.08	1.4602	1.47	129.0	9.96	0.80	+45	1225	4.31	5.29	5.04
	4	H	2	15.9	245-280/0.08-1.7	1.4962	1.41	145.7	12.84	0.71	+5	1300	5.65	3.77	3.54
28	3	H	3	50.0	183-222/0.05-0.1	1.3949	1.58	62.4	7.17	0.77	-25	1150	2.63	3.77	3.54
	4 ^d	H	3	9.7	222-288/0.1-1.7	1.4880	1.42	126.6	11.14	0.70	+5	1200	5.60		
29	2	CH ₃	1	25.1	166-217/0.03	1.4432	1.40	45.3	5.80	0.80	-10	1175			
	2+3	CH ₃	1	63.0	166-261/0.03-0.06	1.4661	1.40	65.9	7.50	0.76	0	1150	3.34	5.61	5.68, 5.79
	3	CH ₃	1	37.9	217-261/0.04-0.06	1.4808	1.36	84.1	8.70	0.76	+5	1200			
	4	CH ₃	1	12.1	261-278/0.06-0.07	1.5115	1.32	172.1	13.0	0.75	+15	1200	4.68	5.56	5.55, 5.55
30	2	CH ₃	2	31.8	180-235/0.08-1.7	1.4371	1.45	75.8	8.29	0.75	-20	1250	3.38	4.65	4.71
	3	CH ₃	2	20.6	235-263/0.08-0.6	1.4722	1.38	125.9	11.26	0.73	-15	1275	4.60		
	4 ^d	CH ₃	2	8.9	261-267/0.6-1.4	1.4919	1.41	165.2	12.97	0.76		1250			
31	2	CH ₃	3	44.7	182-226/0.07-0.08	1.4078	1.55	67.6	7.58	0.76	-20	1200	2.88	3.72	3.73
	3	CH ₃	3	23.3	226-245/0.08-0.09	1.4471	1.45	104.1	10.02	0.74	-20	1250	4.33		
	4	CH ₃	3	11.2	245-264/0.09-0.7	1.4759	1.39	144.9	12.37	0.73	-15	1225	5.28		
32	2	F	1	45.6	180-228/0.05	1.4410	1.52	49.3	6.64	0.75	-25	1175	2.75	5.53	5.37
	2+3	F	1	73.6	180-266/0.05-0.2	1.4575	1.49	56.1	7.56	0.72	-20	1225	3.55		
	3	F	1	28.0	228-266/0.05-0.2	1.4850	1.47	81.7	9.47	0.71	-10	1225	4.44		
	4	F	2	26.8	180-217/0.1-0.3	1.4273	1.56	63.8	8.28	0.71	-25	1225			
33	2+3	F	2	56.1	180-239/0.1-0.2	1.4454	1.54	76.4	9.21	0.71	-20	1250	4.00	4.59	4.10
	3	F	2	29.3	217-239/0.07-0.2	1.4621	1.51	84.9	10.02	0.69	-10	1225			
	4	F	3	19.2	170-195/0.02	1.3797	1.64	52.2	6.88	0.74	-45	1175	1.98		
34	2+3	F	3	65.0	170-217/0.02	1.4061	1.59	61.1	7.70	0.73	-30	1200	3.04	3.72	3.67, 3.77
	3	F	3	45.8	195-217/0.02	1.4154	1.59	67.0	8.22	0.72	-35	1200	3.45		
	4	F	3	16.3	217-262/0.02-0.5	1.4619	1.52	99.3	10.53	0.70	-25	1250	5.58		
35	2	Cl	1	25.9	180-219/0.3	1.4434	1.53	45.7	6.73	0.71	-25	1200	2.52		
	2+3	Cl	1	55.6	180-253/0.3	1.4641	1.52	58.3	7.67	0.71	-25	1250	3.18	5.28	5.21
	3	Cl	1	29.7	219-253/0.2-0.3	1.4822	1.49	73.2	8.98	0.70	-15	1250	3.77		
	4	Cl	1	18.1	253-298/0.2-2.0	1.5135	1.47	119.0	11.39	0.72	+5	1250	4.93		
36	2	Cl	2	18.9	180-203/0.02-0.3	1.3798	1.59	59.3	7.76	0.71	-40	1200	2.20		
	2+3	Cl	2	50.9	180-250/0.02-0.07	1.4041	1.55	76.1	9.31	0.70	-20	1200	3.18	4.30	3.95, 3.90
	3	Cl	2	22.0	203-250/0.03-0.07	1.4152	1.54	88.2	10.15	0.69	-30	1250	3.65		
	4	Cl	2	12.1	250-280/0.07-0.5	1.4622	1.50	123.3	11.71	0.72	-5	1325	4.93		
37	2	H	1	19.7	186-231/0.09	1.4475	1.54	64.6	7.66	0.75	-10	1200	2.34	5.40	5.35
	3	H	1	29.4	231-261/0.08-0.09	1.4868	1.51	127.4	10.85	0.76	+15	1250	3.51		
	4	H	1	26.4	261-304/0.09-0.7	1.5219	1.48	292.5	15.87	0.79	+30	1300	4.71		

^a Not ASTM procedure. See experimental section. ^b Not determined.

^c After standing for several months, this fraction was partly solid.

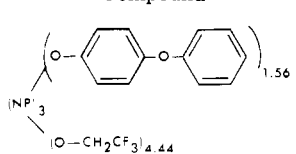
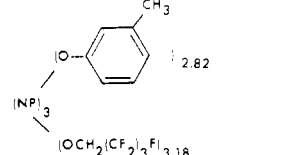
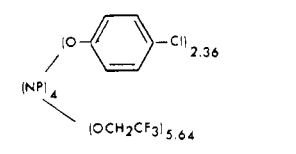
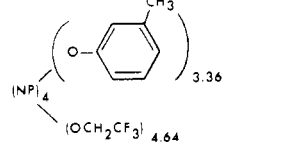
^d After standing for several months, this fraction contained a small amount of solids.

Table III. Hydrolytic Stability of Trimeric and Tetrameric (Aryl-1,1-di-*H*-polyfluoroalkyl)Phosphonitrilates^a

Run No.	Fraction No.	Ring Type, <i>y</i>	Alcohol Type, <i>x</i>	Phenol Type, R	Moles Aryloxy σ	Water Layer, Mg. KOH total	Fluid Layer, Acid No.	Cu Specimen, Wt. Loss, Mg./cm ²
2	3	3	1	H	3.82	0.56	0.01	0.11
6	2+3	3	2	CH ₃	2.67	0.83	0.03	0.068
15	2+3	3	1	OC ₆ H ₅	1.56	0.42	0.01	0.053
18	2+3	3	1	F	2.98	2.37 ^b	0.04	0.039
20	2+3	3	1	Cl	2.89	1.18 ^b	0.02	0.17
25	3	3	1	CF ₃	3.47	1.18 ^b	0.01	0.060
26	2+3	4	1	H	3.51	0.13 ^b	0.01 ^c	0.00
29	2+3	4	1	CH ₃	3.34	2.76	0.04	0.22
31	2	4	3	CH ₃	2.88	0.59 ^b	<0.01	0.00
32	2+3	4	1	F	3.55	1.17	0.06	0.24
35	2+3	4	1	Cl	3.18	2.34	0.04	0.23

^aSpecification MIL-H-19457A (Ships) requires: Water layer total acidity, 5.0 mg. KOH maximum, fluid layer acid number increase, 0.2 maximum, and copper specimen weight loss, 0.3 mg./cm² maximum. ^bTotal alkalinity rather than acidity. ^cNone detectable.

Table IV. Falex Wear Tests^a

Run No.	Fraction	Compound	Time, Hr.	Max. Load, Lb.	Take-up Notches	Journal Condition	Diameter Decrease
15	2+3		8.0	800	54	Scarred	0.001
7	3		8.0	800	36	Slightly scarred	0.001
37	2		8.0	800	140	Scarred	0.003
29	2+3		8.0	800	74	Scarred	0.003

^aUnder identical conditions, tricresyl phosphate gave 142 notches take-up, and diameter decrease of 0.007 inch.

erties were obtained by *m*-substitution, followed, in turn, by *p*- and *o*-substitution.

For the same *a/b* ratio, *m*-fluoro substitution (run 18) gave somewhat lower viscosities, pour points, and spontaneous ignition temperatures than *m*-chloro substitution (run 20). However, there is hardly any difference in physical properties between the two types for the fractions having equal viscosities at 100° F.

Surprisingly, *m*- or *p*-phenoxy substitution (runs 15 and 16) gave relatively low spontaneous ignition temperatures and a *m*-methoxy substituted product (run 14) was even poorer in this respect.

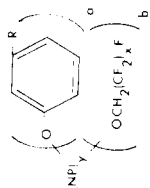
m-Methyl substitution on the phenoxy group (run 5) gave fairly good over-all properties; however, the ASTM

slopes are somewhat marginal and some fractions tended to crystallize. *m*-Trifluoromethyl substitution (run 25) gave good over-all properties, but the ASTM slopes and densities are somewhat inferior to those of the *m*-chloro or *m*-fluoro substituted products (runs 20 and 18). The bulky *p*-*tert*-butyl group (run 13) gave relatively poor properties.

The unsubstituted phenoxy group (runs 1 and 2) frequently resulted in crystalline products. Also, the vapor pressure is relatively high. The corresponding tetrameric product (run 26, Table II) has a relatively low spontaneous ignition temperature.

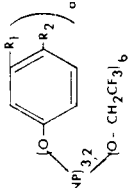
Comparison of Trimeric and Tetrameric Series, (Table I vs. Table II). While the physical properties of the aryl-1,1-di-*H*-polyfluoroalkyl phosphonitrilates were affected by struc-

Table V. Thermal Stability of Trimeric and Tetrameric (Aryl-1,1-di-*H*-polyfluoroalkyl)Phosphonitrilates



Run No.	Fraction No.	Ring Type, <i>y</i>	Alcohol Type, <i>x</i>	Phenol Type, <i>R</i>	Moles Aryloxy <i>a</i>	Kinematic Viscosity, cs.				ASTM Slope		Refractive Index, n_D^{25}		Weight Loss, %
						100° F.	210° F.	Before	After	Before	After	Before	After	
2	3	3	1	H	3.82	79.3	104.7	6.75	8.25	0.87	0.83	1.5050	1.5081	0.58
6	2+3	3	2	CH ₃	2.67	75.8	90.0	5.99	7.01	0.91	0.87	1.4375	1.4396	0.75
12	3+4	3	1	C ₂ H ₅	2.93	54.8	74.1	5.86	7.55	0.84	0.75	1.4773	1.4803	0.40
16	2	3	1	OC ₆ H ₅	1.00	35.7	60.9	4.26	6.53	0.89	0.80	1.4327	1.4366	0.51
18	2+3	3	1	F	2.49	36.8	44.2	4.51	5.45	0.86	0.81	1.4622	1.4638	0.42
20	2+3	3	1	Cl	2.89	56.4	67.4	6.12	6.88	0.83	0.82	1.4909	1.4920	0.10
26	2+3	4	1	H	3.51	57.0	57.0	7.26	6.72	0.74	0.78	1.4652	1.4651	0.52
28	3	4	3	H	2.63	61.9	60.2	7.26	6.79	0.76	0.78	1.3940	1.3937	0.23
31	2	4	3	CH ₃	2.88	67.6	79.9	7.58	8.00	0.76	0.78	1.4078	1.4074	0.21
32	2+3	4	1	F	3.55	56.1	56.6	7.56	7.20	0.72	0.74	1.4575	1.4576	0.49
33	2+3	4	2	F	4.00	76.4	67.2	9.21	8.31	0.71	0.73	1.4452	1.4456	0.50
34	2+3	4	3	F	3.04	61.2	62.9	7.70	7.52	0.73	0.75	1.4061	1.4058	0.18
35	2+3	4	1	Cl	3.18	58.3	58.8	7.67	7.40	0.71	0.74	1.4641	1.4641	0.35
36	2+3	4	2	Cl	3.18	76.1	79.4	9.31	9.01	0.70	0.72	1.4401	1.4394	0.29

Table VI. Aryl-2,2,2-trifluoroethyl Phosphonitrilates Derived from Phosphonitrilic Chloride Mixture



Run No.	Fraction No.	Phenol R ₁	Yield, %	Boiling Point, °C./Mm.	Refractive Index, n_D^{25}	Density, G./Ml.	Kinematic Viscosity, cs.		ASTM Slope	Pour Point, °F.	Spontaneous Ignition, °F. ^a	Aryloxy Content, <i>a</i> ^b	% Nitrogen	
							100° F.	210° F.					Calcd.	Found
38 ^{c,d}	2	CH ₃	31.3	180-221/0.07-0.08	1.4692	1.39	59.8	5.72	0.87	+5	2.70	5.60	5.65, 5.70	
	3	CH ₃	16.3	221-254/0.08-0.18	1.5152	1.30	182.5	10.26	0.86	+30				
39	2	F	30.9	151-180/0.02	1.4282		25.9	3.82	0.86					
	3	F	32.9	180-231/0.02	1.4751	1.48	46.8	5.80	0.81	-10				
	3+4	F	40.0	180-262/0.02-0.04	1.4821	1.47	51.2	6.09	0.80	-5				
	4	F	7.1	231-262/0.02-0.04	1.5169	1.43	89.0	8.32	0.80	+5				
40	2+3	Cl	57.1	180-281/0.03-0.07	1.4884	1.51	61.3	6.54	0.82	-5				
41	2'	Cl	6.1	152-187/0.2-0.5	1.4099	1.55	18.5	3.26	0.86					
	3'	Cl	6.8	187-229/0.5-0.2	1.4636	1.52	44.1	5.44	0.82					
	4'	Cl	29.5	229-341/0.06-0.9	1.5624	1.43	215.7	12.20	0.81	+30				
42	2	H	22.6	180-234/0.07	1.4622	1.55	54.4	5.94	0.83	+5				
	2+3	H	41.4	180-244/0.07-0.08	1.4813	1.51	79.9	6.85	0.84	+5				
	3	H	18.8	234-244/0.07-0.08	1.4981	1.50	110.3	8.17	0.83	+20				
43	2	CF ₃	19.9	152-180/0.03	1.4115									
	3	CF ₃	37.3	180-217/0.03	1.4432	1.52	53.9	5.58	0.85	-5				
	4	CF ₃	13.4	217-240/0.03-1.2	1.4646	1.50	104.4	8.00	0.85	+15				

^aSee a, Table I. ^bCalculated on basis of the trimer (*y* assumed to be 3 in structure III). ^cSpecial procedure, in which xylene replaced ether was used in this run. ^dPartly solid. ^eNot determined. ^fIn run 41, the potassium hydroxide replaced by sodium hydride.

tural modifications, the trends were, in general, independent of the PN-ring size. A direct comparison of the physical properties of the trimeric and the corresponding tetrameric products with an identical a/b ratio shows that the tetramers generally have higher boiling points, viscosities, autogenous ignition temperatures, and thermal stabilities as well as lower ASTM slopes and, frequently, lower pour points.

Utilization of Phosphonitrilic Chloride Trimer-Tetramer Mixture. The most promising runs shown in Tables I and II were repeated using a technical mixture of trimeric and tetrameric phosphonitrilic chloride, containing about 80% trimer. The physical properties of these fluids (Table VI) are not significantly different from those found for the corresponding products which were obtained from either the pure trimeric or tetrameric phosphonitrilic chloride.

In run 41, the experimental procedure was changed slightly, using only sodium hydride as hydrogen chloride scavenger. This gave large amounts of low and high boiling products; the desired middle cut having a viscosity of about 50 cs. at 100° F. was almost entirely absent. The low boilers were stripped with the solvent during the work-up procedure. The high boiling portion (fraction 4) could be distilled without decomposition at a bath temperature of about 450° to 500° C. and contained a high percentage of aryloxy- substituents. While pour point and viscosities of this product are too high for use as a MIL-H-19457-A type fluid, high thermal stability and autogenous ignition temperature (1400° F.) may render this product useful in other applications.

Hydrolytic Stability. One of the most important property requirements for naval hydraulic fluids is hydrolytic stability. Previous experience with similar compounds (5, 6) has shown that special purification techniques are essential to obtain materials passing the hydrolytic stability test outlined in MIL-H-19457-A (Ships) (7). These methods, designed for the removal of even traces of unreacted starting materials, such as phenol and fluoroalcohols, of acidic impurities and products resulting from incomplete substitution of the chlorine atoms attached to the phosphonitrilic ring, were also successfully employed for the compounds of structures IIIa and IIIb.

The performance of several phosphonitrilate fluids of structures IIIa and IIIb under the conditions of the hydrolytic stability test is summarized in Table III.

Thermal Stability. The fluids which emerged from the thermal stability test (Table V) were usually much darker in color but contained only small amounts of solid deposits. The weight losses, which varied from 0.10 to 0.75%, were considerably lower than those observed for phosphonitrilates containing 1,1, ω -tri-*H*-polyfluoroalkyl groups (5, 6). The viscosities of the trimeric products had slightly increased after the test, while the ASTM slopes had decreased. Both changes indicate partial conversion of the trimers to tetrameric products, previously also observed for compounds of structure Ia (10). With only a few exceptions, the viscosities of the tetramers remained unchanged, which is considered an indication that the tetrameric aryl-1,1-di-*H*-polyfluoroalkyl phosphonitrilates are the thermally more stable species. Minor differences in the infrared spectra before and after the test were noted.

Falex Wear Test. The performance of several aryl-1,1-di-*H*-polyfluoroalkyl phosphonitrilates in the Falex wear test is summarized in Table IV. From the results, it is easily recognized that all compounds (IIIa and IIIb) tested were appreciably better than tricresyl phosphate which was used as standard.

CONCLUSION

Replacement of the terminal hydrogen atoms in aryl-1,1, ω -tri-*H*-polyfluoroalkyl phosphonitrilates (IIa and IIb) by fluorine resulted in products (IIIa and IIIb) having considerably lower viscosities. If the chain length of the 1,1-di-*H*-polyfluoroalkyl groups was kept short, the products (III, $n = 1, 2, \text{ or } 3$) had densities below 1.6. Several of these new products (IIIa and IIIb, $x = 1 \text{ to } 3$) meet the requirements for MIL-H-19457-A (Ships) type fluids with regard to all properties discussed in this paper. Preliminary high pressure ignition tests indicate that representative compounds of type III can be expected to pass the compression ignition test (1, 2, 7). Further improvement in properties should be possible by formulating these fluids.

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