to the original organic phase and dried over magnesium sulfate.

Next, 2-chlorocyclohexane (484 grams, 3.65 moles) was dissolved in ether and added dropwise to a stirred suspension of sodium methoxide (213 grams, 3.94 moles) in dry ether (1200 ml.). After complete addition, the mixture was stirred with refluxing for 2 hours and then cooled. Water was added to dissolve the salts and the two layers were separated. The aqueous layer was extracted twice with 100-ml. portions of ether, the combined extracts being washed with 5% hydrochloric acid, 5% bicarbonate, and saturated sodium chloride solution and then dried over magnesium sulfate. Distillation afforded 284 to 302 grams (61 to 65%) of ester, 75–77°/48 mm. (*5*).

3-Hexyl-1,6-hexanediol and 3-"Octyl"-1,6-hexanediol (*4*). 3-Hexyl-1,6-hexanediol. β-Hexyladipic acid (*4*) was reduced with lithium aluminohydride in ether according to standard procedure to give an 80% yield of glycol (b.p., 137–40°/0.4 mm.). Phosphorus tribromide in the usual manner afforded the 1,6-dibromide in 61% yield (b.p., 114–7°/0.1 mm.).

3-"Octyl"-1,6-hexanediol. The standard lithium aluminohydride reduction of β-"octyl" adipic acid (*4*) in ether afforded an 88% yield of glycol (b.p., 154–7°/0.25 mm.). Conversion in the usual manner by means of phosphorus tribromide afforded a 39% yield (b.p., 124–6°/0.1 mm.).

In connection with this phase of the work, the problem of corrosion of copper by sulfur compounds was encountered. Inasmuch as there are reports in the literature that certain selenides are effective antioxidants, and the impurities arising in the course of selenide preparation are more readily removed than their sulfur analogs, it was thought that the frequently observed extensive corrosion of copper and attendant decomposition of organic sulfides might be attributable to dissolved traces of hydrogen sulfide or mercaptans. Accordingly, a sample of 1,6-bis(2′-ethylhexylthio)hexane was prepared in the usual manner and carefully distilled through a Claisen head. Neither copper nor a mixture of copper and iron was attacked during heating for 15 to 24 hours at 150° in a nitrogen atmosphere. A thorough washing of the sulfides in diethyl ether with 10% aqueous copper sulfate, followed by filtration, also was an effective way of preliminary purification. It was especially useful in purification of selenides.

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Structural Guides to the Development of High Dielectric Constant Esters for Capacitors

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THE NEED FOR dielectric liquids that may be used over a much wider range in temperature than heretofore has been recognized for some time and certain military requirements have been established for such materials to be used from −65° to 200° C. (*44*). In addition, low-loss liquids of higher dielectric constant than those now used would permit the design of smaller and lighter equipment components. Present commercially available dielectric liquids do not have dielectric constants much higher than 5.

If a dielectric liquid is to be used in a wide temperature range, it must be stable toward oxidation and resistant to thermal breakdown at high temperatures. Volatility must be low in order to prevent loss of the capacitor impregnant under high-temperature conditions. At low temperatures, the liquid must not crystallize or become extremely viscous, as this results in a reduction in dielectric constant, accompanied by an increase in dielectric losses. To maintain the long life of liquid-impregnated capacitors, it is essential that the liquid be stable toward hydrolysis and incapable of reaction with the capacitor metal electrodes under conditions of high temperature and electrical stress. It is also desirable that dielectric liquids be flame-resistant and have high flash points.

A number of partially fluorinated esters, synthesized for use as high-temperature lubricants and hydraulic fluids, were found to have unusual chemical, physical, and electrical properties that made them promising as capacitor impregnants (*10, 28*).

One of the partially fluorinated esters was tested as a capacitor impregnant (*5*) and found to give substantial improvement over existing commercial dielectric liquids. This led to an investigation of the factors involved in the formulation of dielectric liquids having high dielectric constants. The survey included a study of composition, molecular structure, and dipole moment of a large number of compounds and resulted in the development of methods for estimating the dielectric constant of new, unsynthesized compounds. This report outlines such methods and their use in planning syntheses of a number of partially fluorinated esters with dielectric constants above eight.

ELECTRICAL PROPERTIES OF LIQUIDS

Characteristics of a dielectric liquid which are of major importance include dielectric constant (sometimes referred to as specific inductive capacity), electrical loss, and electrical breakdown strength. The property of interest to this report is the relative dielectric constant, a dimensionless number ϵ, the value of which is determined by measuring the ratio of the electrical energy which may be stored in a capacitor having a given medium between the plates to that which may be stored in the same capacitor, at the same voltage, with a vacuum between the plates.

When the positive and negative charges in the atoms and molecules of a dielectric liquid are displaced by the action of an electric field, the phenomenon is known as polarization. This is a fundamental property of materials. The dielectric constant is a function of the polarizability of a substance. The total polarizability is composed of interfacial, electronic, atomic, and orientation or permanent dipole polarizabilities and varies with frequency. These properties are discussed fully in standard works on dielectric behavior (*2, 31, 45*). Dipole polarization arises because certain molecules possess an asymmetry of change distribution between unlike members of the molecule, so that a permanent electric moment exists, even in the absence of a field. When a field is applied, the molecule aligns itself under torque, thus storing electrical energy that will be released when the applied field is removed. Since electronic and atomic polarizations do not vary widely in different polar liquids and the principal contribution to the total dielectric constant arises from dipole polarization, the permanent dipole moment is the major factor to be considered in developing high dielectric constant liquids.

DETERMINATION OF DIPOLE MOMENTS

Dipole moments of polar molecules may be determined directly from measurements of the dielectric constant of the material in the gaseous or vapor state, or with somewhat less certainty, by extrapolation of results from measurements on dilute solutions in a nonpolar solvent such as benzene. The gas method requires high precision in electrical measurements and implies a substantial volatility of the polar compound. The solution method, while more general, is subject to interference from the interaction of dipoles with solvent, requires high-precision measurements on several solutions, and involves extrapolation of nonlinear data to zero concentration of the polar solute.

There have been numerous attempts to calculate the dipole moment of the isolated molecule directly from dielectric constant measurements on pure liquids. The equations of Mosotti, Clausius, and Debye work well with relatively nonpolar liquids. They do not hold for strongly polar liquids in which the electrical interaction of the dipoles has a major effect on the total polarizability. Onsager (*23*) has developed an equation based on theoretical considerations, which is moderately successful in relating the dipole moment of polar molecules to their bulk liquid dielectric constant (*32*). Spherical molecules with point dipoles at their centers are assumed. The general agreement between dipoles calculated from the Onsager equation and those derived from measurements in the gaseous phase or on solutions is of the order of 5%, in most cases. The equation is not applicable to strongly associated compounds such as water or alcohol. Others have refined or modified the Onsager equation (*33*) by consideration of further variables, but, while the over-all agreement is somewhat improved, the difficulties in computation are multiplied. In most cases, estimates from the original Onsager equation are as useful as those from the later equations or even the moments calculated from solution measurements.

The Onsager equation (*34*) is

$$\mu^2 = \frac{9KT}{4\pi N} \left\{\frac{M}{d}\right\} \left\{\frac{(2\epsilon + \epsilon_\infty)(\epsilon + 2)}{3\epsilon(\epsilon_\infty + 2)}\right\} \left\{\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_\infty - 1}{\epsilon + 2}\right\} \quad (1)$$

where

μ = permanent dipole moment in electrostatic units (esu); 1×10^{-18} esu equals 1 debye, D
K = Boltzmann's constant, 1.38×10^{-16} erg per degree
N = Avogadro's number 6.023×10^{23}, number of molecules in a mole
T = absolute temperature in degrees Kelvin
M = molecular weight in grams per mole
d = density in grams per cubic centimeter
ϵ = dielectric constant
ϵ_∞ = dielectric constant at infinite frequency

In this report, the square of the index of refraction for visible light (*D*-line of sodium) is substituted for ϵ_∞ (*3*). The equation may also be expressed in such a way that ϵ appears as an explicit function of $\mu^2 d/M$ and the square of the refractive index, n^2:

$$2\epsilon^2 - \epsilon\left\{n^2 + (n^2 + 2)^2 \frac{\mu^2 d/M}{9KT/4\mu N}\right\} - n^4 = 0 \quad (2)$$

This equation is a quadratic in ϵ which may be solved when definite values are assigned for the remaining variables, n^2 and $\mu^2 d/M$. A nomograph for the rapid and convenient solution of Onsager's equation may be prepared by plotting ϵ as a function of $\mu^2 d/M$ for several appropriate values of n^2 (or n), as is shown in Figure 1. The quantity $\mu^2 d/M$—i.e., μ^2/ molar volume—may be taken as a convenient indication of dipole moment density in the liquid. It is clear that the Onsager equation can be used conveniently for predicting the dielectric constants for new compounds if reliable estimates can be made for their refractive index, density, and permanent dipole moment. Given this information, one calculates $\mu^2 d/M$ and reads from Figure 1 the appropriate value of ϵ for the estimated index of refraction. Of the three physical constants required, the refractive index can be predicted from well-established tables of atomic refractivity (*35*) and the densities either by analogy to known compounds or from molecular parachors (*26, 42, 43*). The estimate of dipole moments for large and complex organic molecules, however, is on no such firm footing, and requires more extended consideration.

PREDICTION OF DIELECTRIC CONSTANTS FOR ESTERS BEFORE SYNTHESIS

The time and expense involved in the synthesis of new compounds in the quantity and purity required for their study as high dielectric constant liquids for capacitors are considerable. Reliable estimates of stability, liquidus range, and probable electrical properties should be available if an effective synthetic program is to be planned. Previous experience in the synthesis of extreme-temperature lubri-

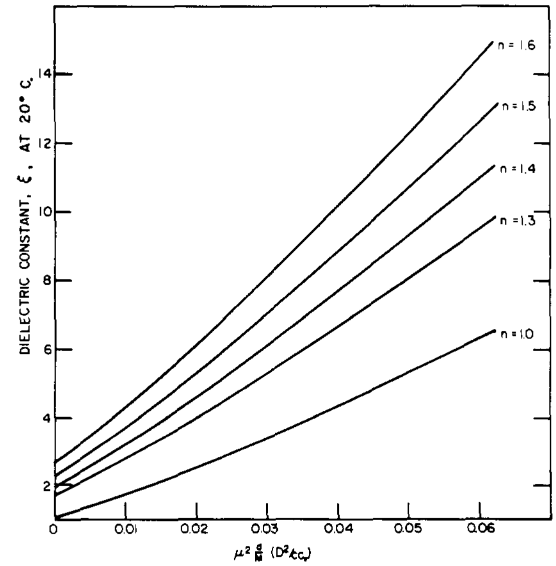


Figure 1. Nomograph for graphic solution of the Onsager equation

cants has provided an excellent basis for the prediction of chemical stability, viscosity-temperature coefficient, and volatility (*22*). This report attempts to establish a basis for comparably reliable predictions about dielectric constant.

Some qualitative but very useful guidance may be drawn from the nature of the basic equations of Debye and of Onsager. The dielectric constant is a function of polarization per unit volume, which may be increased if the concentration of dipoles per cubic centimeter is increased. Since to a first approximation, the members of a homologous ester series have equal dipole moments, the desired effect may be secured by using the ester containing the smallest alcohol moiety and the shortest dibasic acid compatible with the practical requirement of low volatility. More of these molecules will be contained in each cubic centimeter. Somewhat less important gains may be achieved by choosing an aromatic acid, which increases the electronic polarizability, as can be seen from the increase in refractive index. Further gains are possible by increasing the number or changing the relative position of the fluoroester groups in each molecule. Such changes may increase the number of dipoles per cubic centimeter without increasing volatility.

Estimation of Dipole Moments from Structure. The accurate prediction of dipole moments for such complex molecules, on the basis of the proposed structure, is beset with formidable difficulties. It is possible to account quantitatively for the dipole moments of small rigid molecules, such as methane and the chloromethanes (*36*), and the somewhat more complex molecules in which several dipole elements are associated with atom groups free to rotate in fully specified modes (*37*). With the number of polar components and the degrees of rotational freedom permissible with

Table I. Dipole Moments of Alkyl Monoesters of Aliphatic Acids

No.	Compound	Dielectric Constant,^{a} ϵ	Onsager Dipole Moment, μ, in Debye Units, D	Measured Dipole Moment, μ, in Debye Units, D^b	$\mu^2 d/M$, D^2 Cc.$^{-1}$ (Onsager)	Refs.
1	Methyl formate	8.5	1.74	. . .	0.0492	(*47*)
2	Ethyl formate	7.16 (25° C.)	1.79	1.92v 1.94s	0.0398	(*47, 39*)
3	Propyl formate	7.7^c (19° C.)	2.01	1.89s	0.0413	(*47, 39*)
4	Isobutyl formate	6.4^c (19° C.)	1.93	1.88s	0.0323	(*47, 39*)
5	Amyl formate	5.7 (19° C.)	1.88	1.90v	0.0327	
6	Methyl acetate	6.79	1.69	1.67v 1.74s	0.0363	(*18, 47, 39*)
7	Ethyl acetate	6.02 (25° C.)	1.72	1.76v 1.86s	0.0300	(*47, 39*)
8	Propyl acetate	5.69 (19° C.)	1.78	1.82s	0.0276	(*47, 39*)
9	Butyl acetate	5.01	1.73	1.84s	0.0226	(*47, 39*)
10	Amyl acetate	4.75	1.75	1.75v	0.0205	(*47, 17*)
11	Benzyl acetate	5.1^d (21° C.)	1.59	. . .	0.0177	(*47*)
12	Methyl propionate	5.5^c (19° C.)	1.60	1.69s	0.0267	(*14, 39, 18*)
13	Ethyl propionate	5.65 (19° C.)	1.74	1.81s	0.0274	(*47, 39*)
14	Propyl propionate	4.7^d	1.65	1.77s	0.0206	(*14, 18, 39*)
15	Isoamyl propionate	4.2^d	1.66	. . .	0.0167	(*15, 18*)
16	Methyl butyrate	5.6^d (19° C.)	1.75	1.71s	0.0268	(*14, 18, 39*)
17	Ethyl butyrate	5.10 (18° C.)	1.75	1.74s	0.0233	(*14, 18, 39*)
18	Propyl butyrate	4.3^d	1.62	. . .	0.0176	(*14, 18*)
19	Isobutyl butyrate	4.1^d	1.64	. . .	0.0161	(*14, 18*)
20	Isoamyl butyrate	4.0^d	1.68	. . .	0.0153	(*14, 18*)
21	Methyl valerate	4.3^d	1.52	1.74s	0.0178	(*9, 18, 39*)
22	Ethyl valerate	4.69	1.74	. . .	0.0202	(*14, 18*)
23	Propyl valerate	4.0^d (19° C.)	1.60	. . .	0.0154	(*15, 18*)
24	Isobutyl valerate	3.8^d (19° C.)	1.61	. . .	0.0083	(*15, 18*)
25	Isoamyl valerate	3.6^d (19° C.)	1.57	. . .	0.0127	(*15, 18*)
26	Ethyl laurate	3.44	1.64	. . .	0.0102	(*14, 18*)
27	Ethyl palmitate	3.20	1.70	1.87s	0.0087	(*9, 14, 18*)
28	Butyl stearate	3.11 (30° C.)	1.85	. . .	0.0083	(*47*)

[a] At 20° C. and audio-frequency, unless otherwise indicated. [b] s = solution v = vapor. [c] At 4 × 10^8 cps. [d] At 5 × 10^8 cps.

Table II. Dipole Moments of Alkyl Esters of Aromatic Acids

No.	Compound	Dielectric Constant,^{a} ϵ	Onsager Dipole Moment, μ, in Debye Units, D	Measured Dipole Moment, μ, in Debye Units, D^b	$\mu^2 d/M$, D^2 Cc.$^{-1}$ (Onsager)	Refs.
1	Methyl benzoate	6.59	1.81	1.83s	0.0262	(*39, 47*)
2	Ethyl benzoate	6.02	1.84	1.82s 2.00v	0.0236	(*8, 17, 44*)
3	Isobutyl benzoate	5.38	1.91	. . .	0.0204	(*15, 18*)
4	Amyl benzoate	5.00	1.88	. . .	0.0182	(*15, 18*)
5	Benzyl benzoate	4.9^c	1.68	. . .	0.0148	(*14, 47*)
6	Dimethyl phthalate	8.5 (24° C.)	2.47	. . .	0.0373	(*15, 18, 30*)
7	Dibutyl phthalate	6.63	2.71	2.75s	0.0277	(*6, 18, 47*)
8	Dioctyl phthalate	5.1 (25° C.)	2.79	. . .	0.0195	(*18, 30*)
9	Diethylhexyl phthalate	5.3	2.84	. . .	0.0203	NRL (*24*)
10	Diethylhexyl terephthalate	4.5	2.47	. . .	0.0154	NRL
11	Diethylhexyl tetrahydrophthalate	4.5	2.58	. . .	0.0163	NRL

[a] At 20° C. and audio-frequency, unless otherwise indicated. [b] s = solution; v = vapor. [c] At 4 × 10^8 cps.

Table III. Dipole Moments of Alkyl Diesters of Aliphatic Acids

No.	Compound	Dielectric Constant,[a] ϵ	Onsager Dipole Moment, μ, in Debye Units, D	Measured Dipole Moment, μ, in Debye Units, D[b]	$\mu^2 d/M$, D^2 Cc.$^{-1}$ (Onsager)	Refs.
1	Diethyl oxalate	8.1[c](21° C.)	2.37	2.51s	0.0415	(*39, 47*)
2	Dimethyl malonate	10.4	2.51	. . .	0.0554	(*15, 18*)
3	Diethyl malonate	8.18	2.51	2.56s	0.0417	(*18, 39, 44*)
4	Dimethyl succinate	5.1	1.70	. . .	0.0220	(*15, 18*)
5	Diethyl succinate	6.74	2.33	2.30v 2.14s–2.21s	0.0324	(*14, 18, 39*)
6	Diethyl glutarate	6.93	2.47	2.42s	0.0333	(*14, 18, 39*)
7	Diamyl glutarate	5.03[d]	2.44	2.31s	0.0208	(*29*)
8	Diheptyl 3-methylglutarate	4.35[d]	2.45	2.23s	0.0162	(*29*)
9	Dinonyl glutarate	4.0	2.41	. . .	0.0138	NRL
10	Diethyl azelate	5.29	2.38	. . .	0.0256	(*9, 15, 18*)
11	Diethyl sebacate	5.12	2.39	2.49s	0.0214	(*9, 14, 18, 39*)
12	Dibutyl sebacate	4.65	2.48	. . .	0.0182	(*18, 44*)
13	Dioctyl sebacate	4.06	2.57	. . .	0.0141	(*18, 24*)
14	Dipropylene glycol dipelargonate	4.7	2.87	. . .	0.0188	NRL
15	Dihexyl pinate	4.5	2.51	. . .	0.0168	NRL(*19*)

[a] At 20° C. and audio-frequency, unless otherwise indicated. [b] s = solution; v = vapor. [c] At 4 × 10^8 cps. [d] At 10^6 cps.

Table IV. Dipole Moments of Alkyl Tri- and Tetraesters of Aliphatic Acids

No.	Compound	Dielectric[a] Constant, ϵ	μ, in[b] Debye Units, D	$\mu^2 d/M$, D^2, Cc.$^{-1}$	Refs.
1	Tri-*n*-butyl tricarballylate	5.7	2.95	0.0253	NRL(25)
2	Triisoamyl tricarballylate	5.1	2.85	0.0212	NRL
3	Pentaerythritol tetrapelargonate	3.05	2.35	0.0071	NRL

[a] At 20° C. and audio-frequency.
[b] Onsager dipole moment.

polyesters, however, rigorous prediction is not yet possible. Pentaerythritol tetrapelargonate, which an organic chemist classifies as symmetrical, has a dipole moment of 2.35. The molecule is not electrically symmetrical, as is tetrachloromethane, because only a very few of the configurations possible by random rotation of the four groups about bonds adjacent to the carboxyl are such as to give complete cancellation of the dipole moments of these groups. All other patterns produce a resultant moment for the molecule.

In the case of two or more unit or group dipoles which are connected by a molecular linkage so flexible that the orientation of one is completely random with respect to the other, the relation

$$\mu^2 = Z\mu_0^2 \qquad (3)$$

or

$$\mu = Z^{1/2}\mu_0$$

applies (*38*). Here μ_0 is the moment of the unit or group dipole which is repeated, and Z is the number of dipoles. When complete randomness of orientation cannot prevail, Debye and Bueche (*7*) have suggested an equation $\mu^2 = FZ\mu_0^2$, in which F is a number less than unity which reflects the effects of restricted rotation. Unfortunately, the knowledge of motions possible to parts of a complex molecule is not yet adequate for prediction of the factor F. One must, therefore, fall back on more or less empirical generalizations about the relations of structure to dipole moment for guidance in the synthesis of new molecules.

As a basis for such generalizations the authors have assembled dielectric constant data and, when available, measured dipole moment data for a large number of esters as well as for some selected compounds of other structural types. In all cases, the dipole moment of each compound has also been calculated by Onsager's equation from the dielectric constant of the pure liquid. These calculated dipole moments are used as a basis for all structural generalizations and predictive procedures described.

To establish the effects of specific structural modifications on dipole moments, the compounds studied have been grouped into six categories in Tables I to VI. The ratio of the average Onsager dipole moment of the aliphatic diesters to that of the monoesters agrees well with the value predicted by Equation 3. The ratio of the dipole moments of the tricarballylate esters of amyl and butyl alcohol to the average moment of the monoesters agrees reasonably with that expected for fully random orientation. In the fluorine-substituted esters, replacement of the hydrocarbon alkyl group with the $H(CF_2)_n—CH_2—$ group raises the dipole moment of the monoester appreciably. This effect results largely from the introduction of the $—CF_2H$ terminal group. If this is replaced by a $—CF_3$ group, the moment of the diester is reduced. Fluoroalkyl groups having $—CF_2H$ and $—CF_3$ terminal groups are designated in this report as ψ' and Φ', respectively, after the system used by others (*10*).

When the effect of additional ψ' fluoroester groups in a single molecule is considered, it is noted that the moment ratios for the di-, tri-, and tetraesters fall further below those predicted for random orientation than those of the corresponding aliphatic types (Table VII). This may be because the $H(CF_2—CF_2)_nCH_2OC(:O)—$ group has been treated as equivalent to a rigid dipole unit, in analogy to the $ROC(:O)—$ group of the nonfluorinated esters. However, the $—CF_2H$ terminal group may function as a more or less independent dipole attached through the flexible methylene linkage adjacent to the ester group. In this case, one deals with a molecule containing four dipoles of two kinds, for which the general treatment (*40*) would predict a lower resultant moment.

The relations between the number of ester groups per molecule and the ratio of moments for the polyester and the corresponding monoester of aliphatic acids are summarized in Table VII. Increasing the dielectric constant by increasing the number of ester groups per molecule is of dubious utility after the introduction of the third ester group.

If two dipole-containing groups are located on one side of a rigid molecule, the resultants of their averaged dipole vectors may reinforce each other strongly, as in the case of *o*-dichlorobenzene. The gain from such forced cooperation is reduced in the aromatic esters because of intramolecular rotation of the individual dipoles present. This behavior is illustrated by benzene compounds substituted with rotatable dipole groups in the 1, 2- or 1, 2, 3-positions.

Table V. Dipole Moments of Fluoroalkyl Esters of Aliphatic Acids

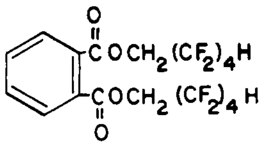
No.	Compound^a	Dielectric Constant,^{b} ϵ	Onsager Dipole Moment, μ, in Debye Units, D	$\mu^2 d/M$, D^2 Cc.$^{-1}$	Refs.
1	ψ'-Nonyl 2-ethylhexanoate	4.66^c	2.93	0.0221	*(28)*
2	Bis(ψ'-heptyl) 2-phenylsuccinate	5.60	3.69	0.0272	NRL(*20*)
3	ψ'-Heptyl hydrogen 3-methylglutarate	5.49	2.83	0.0270	NRL
4	Bis(ψ'-amyl) glutarate	7.48^c	3.80	0.0413	*(28)*
5	Bis(ψ'-propyl) 3-methylglutarate	8.85	3.52	0.0486	NRL
6	Bis(ψ'-amyl) 3-methylglutarate	7.44^c	3.88	0.0408	*(28)*
7	Bis(Φ'-hexyl) 3-methylglutarate	4.20	2.94	0.0195	NRL(*10*)
8	Bis(ψ'-heptyl) 3-methylglutarate	5.94^c	3.83	0.0312	*(28)*
9	Bis(φ'-octyl) 3-methylglutarate	3.81	3.01	0.0168	NRL(*10*)
10	Bis(ψ'-heptyl) 2-phenylglutarate	5.34	3.61	0.0253	NRL(*20*)
11	(ψ'-amyl/ψ'-heptyl/ψ'-nonyl)dicamphorate	5.39	3.69^d	0.0263	NRL(*1, 13*)
12	Tris(ψ'-propyl) tricarballylate	10.8	4.51	0.0610	NRL
13	Tris(ψ'-amyl) tricarballylate	7.81^c	4.60	0.0433	*(28)*
14	Tetrakis(ψ'-amyl) 1,2,3,4-butane tetracarboxylate	5.24 (77° C.)	4.64^e	0.0331	NRL

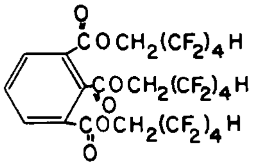
[a] Fluoroalkyl groups having $-CF_2H$ and $-CF_3$ terminal groups are designated in this report as ψ' and φ', respectively, after the system used (*10*).
[b] At 20° C. and audio frequency, unless otherwise indicated. [c] At 10^6 cps. [d] Calculated as ψ'-heptyl ester.
[e] Based on estimated density and index of refraction data.

Table VI. Dipole Moments of Fluoroalkyl Esters of Aromatic Acids

No.	Compound	Dielectric Constant,^{a} ϵ	Onsager Dipole Moment, μ, in Debye Units, D	$\mu^2 d/M$, D^2 Cc.$^{-1}$	Refs.
1	ψ'-Amyl benzoate	8.19	3.08	0.0415	NRL
2	ψ'-Heptyl *o*-phenoxybenzoate	7.60	3.52	0.0354	NRL
3	2,2,3,3,4,4-Hexafluoro-1,5-pentanediol dibenzoate	6.73	2.95	0.0284	NRL
4	Bis(ψ'-amyl) *o*-phthalate	8.67^b	4.11	0.0459	*(28)*
5	Bis(ψ'-amyl) *m*-phthalate	7.87	3.86	0.0406	NRL
6	Tris(ψ'-amyl)benzene 1,2,3-tricarboxylate	8.98	4.91	0.0482	NRL
7	(ψ'-amyl/ψ'-heptyl)benzene 1,2,4,5-tetracarboxylate	5.31	4.25^c	0.0252	NRL(*1*)
8	Bis(ψ'-propyl) diphenate	9.70	3.84	0.0451	NRL
9	Bis(ψ'-amyl) diphenate	8.0	4.06	0.0384	NRL(*20*)

[a] At 20° C. and audio frequency, unless otherwise indicated.
[b] At 10^6 cps.
[c] Calculated as ψ'-hexyl ester.





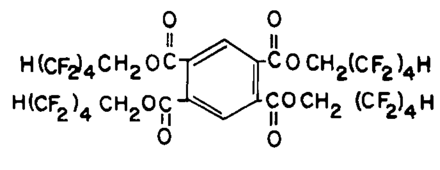
The ψ'-amyl *o*-phthalate, which has two ester groups attached at points 60 degrees apart on the ring, shows $\mu_2/\mu_1 = 1.33$, when μ_1 is taken as the moment of ψ'-amyl benzoate. The effect of cooperative orientation is in this case slight, since $\mu_2/\mu_1 = 1.27$ for fluoroesters of dibasic and monobasic aliphatic acids, in which no forced orientation is expected. The ratio, μ_2/μ_1 for aliphatic esters of *o*-phthalic and benzoic acids, respectively, on the other hand, is 1.53. This indicates a substantial gain in dipole moment from ortho-located ester dipoles, although it is less than the ratio of 1.62 between the moment of *o*-dichlorobenzene and monochlorobenzene. The smaller gain from cooperative orientation in the case of the *o*-phthalate fluoroesters than with aliphatic esters is attributed to flexibility in the fluoroalkyl radical (particularly at the $-CH_2-$ linkage) which permits further randomness of directions for the terminal $-CF_2H$ dipoles.

In the case of the fluoroester of hemimellitic acid (1,2,3-benzenetricarboxylic acid), the accumulation of three fluoroester groups on one side of the molecule results in a ratio $\mu_3/\mu_1 = 1.59$. This is very nearly the value for the fluoroesters of tricarballylic acid, for which no forced orientation seems likely.

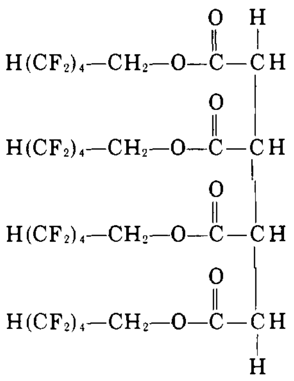
Table VII. Averaged Effect of Number of Ester Groups Present on Dipole Moment of Noncyclic Esters

	Moment Ratio, μ_n/μ_1		
Ester Type	Calcd. for random orientation	Found, aliphatic esters	Found, aliphatic ψ'-fluoroesters
Diester	1.41	1.41	1.27
Triester	1.73	1.68	1.56
Tetraester	2.0	. . .	1.58

The ψ' fluoroester of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) has two adjacent ester groups opposing two identical groups across the ring.



The ratio, μ_4/μ_1, of the dipole moment of this compound to that of the ψ'-amyl benzoate monoester is 1.38 as compared to 1.58 for the fluoroester of 1,2,3,4-butanetetracarboxylic acid. The observed dipole moment of 4.25D for the "symmetrical" ester, however, is far from the zero moment of the formally analogous 1,2,4,5-tetrachlorobenzene. It is evident that there are many configurations open to the component dipoles of the ψ' fluoroesters as a result of intramolecular thermal motion and that only small gains can be expected from constraints imposed by relative position on the aromatic nucleus.



In the course of this investigation other types of fluorinated organic molecules were examined. The results are reported in Table VIII. The compounds were not stable enough for consideration as capacitor liquids, but their properties give further information on the relation of structure to dielectric constant. The substituted silanes containing ψ'-fluoroalkyl groups are of interest because their moments and dielectric constants are so much greater than those of nonfluorinated analogs. Three examples of the latter are given for comparison. It is apparent that in the silane compounds the $—CF_2H$ dipole has much randomness of orientation, whereas the dipoles associated with the $Si—O—CH_2—$ linkages are restricted as to possible orientations, and so cancel each other.

Effects of Electronic Polarization. Figure 1, which summarizes the relation between μ^2d/M and the dielectric constant for various values of the refractive index, stresses the importance of high electronic polarization in conferring a high dielectric constant on liquids having polarities comparable to the esters considered here. The numerical effect becomes larger as μ^2d/M increases, so that for a high value of μ^2d/M, 0.05, the dielectric constant would be increased from 8.0 to 12.2, if the refractive index were changed from 1.3 to 1.6. This is approximately a 50% gain. From this point of view, the presence of fluorine atoms, with their low electronic polarizability, is a handicap, and the fluorine content should obviously be kept as low as possible. This can be done if one uses the ψ'-fluoropropyl group. The gain in refractive index and in the value of μ^2d/M resulting when this group is substituted for ψ'-fluoroamyl or ψ'-fluoroheptyl groups strongly outweighs the slightly smaller group moment of the ψ'-fluoropropyl group which is revealed by a careful examination of Tables V and VI. Aromatic structures, on the other hand, increase the index of refraction. Hence, aromatic acids are attractive not only because of the modest possibilities for cooperative orientation of the dipoles, but because of the large increase in electronic polarizability which they introduce. The presence of other easily polarized atoms, such as chlorine, makes a valuable contribution to polarizability. Aroclor 1254, which approximates a pentachlorodiphenyl, has an Onsager dipole moment of only $1.67D(\mu^2d/M = 0.0130)$, but its refractive index of 1.64 results in a dielectric constant of 5.0 instead of the 3.5 characteristic of aliphatic esters having the same μ^2d/M (Figure 1).

STRUCTURAL GUIDES FOR SYNTHESIS OF HIGH DIELECTRIC CONSTANT LIQUIDS

For a given dipole structure, the molecular volume should be the minimum compatible with the low volatility required. The volatility of organic liquids in general may be reduced by increasing molecular weight or the number of polar groups per molecule.

The nonfluorinated portions of the molecule should be chosen to provide the highest practicable index of refraction, by the use of aromatic acids and/or by the inclusion of stable chlorine substituents.

The dipole moment should be as high as possible with respect to molecular volume; thus $\mu^2/(M/d)$ should be high. Dipole moments are affected by the following considerations: Esterifying alcohols contribute to the dipole effect in the order: telomeric fluoroalcohols > perfluoroalcohols > aliphatic alcohols. The introduction of a second ester group into a flexible molecule increases the dipole moment by 25 to 40%; the introduction of two additional ester groups gives an increase of 50 to 60%. Beyond this point, the introduction of additional ester groups increases the volume of the molecule sufficiently to cancel the effect of the small increase in moment on the dielectric constant. Given a suitable rigid element in the molecular structure, some gain in dipole moment can result from structurally forced cooperation of component dipoles, as in the *o*-phthalate or hemimellitate esters, but these gains are smaller for ψ' fluoroesters than for analogous nonfluorinated esters, and much smaller than for the case of simple nonrotatable dipoles. Members of a strictly homologous series exhibit approximately equal dipole moments.

The viscosity-temperature coefficient should be small—i.e., the liquid should have an acceptable viscosity over a wide temperature range. This can be achieved by selection of nonassociated compounds whose molecules are flexible, and which exhibit wide differences in their major linear dimensions between the most compact and the most extended configurations they can assume. These considerations were discussed in detail in an earlier publication (*22*).

Estimation of Refractive Index and Density of Proposed Molecular Structures. The estimation of the dielectric constant of a new organic liquid from the expected dipole moment by means of the Onsager equation and the relationships shown in Figure 1 also requires an estimate of the refractive index and density of the new compound. In view

Table VIII. Dipole Moments of Miscellaneous Halogenated Compounds

No.	Compound	Dielectric Constant,[a] ϵ	Onsager Dipole Moment, μ, in Debye Units, D	μ^2d/M, D^2 Cc.$^{-1}$	Refs.
1	Bis(ψ'-heptoxy) hexane	9.4	5.10	0.0550	NRL(*10*)
2	Bis(*tert*-butoxy) bis(ψ'-heptoxy) silane	6.61	4.44	0.0344	NRL
3	Bis(*tert*-butoxy) bis(ϕ'-octoxy) silane	4.85	3.90	0.0247	NRL
4	Bis(3,3,4,4-tetrafluoro-2-methyl-2-butoxy) bis(ψ'-heptoxy) silane	7.01	4.89	0.0392	NRL
5	Tetrakis (1-trifluoromethyl heptoxy) silane	4.10	3.70	0.0164	NRL
6	2-Ethylhexyl silicate	2.50	1.48	0.0035	NRL
7	Hexa-2-ethyl-1-butoxy disiloxane	2.92	2.25	0.0068	NRL
8	Hexa-4-methyl-2-pentoxy disiloxane	2.80	2.16	0.0062	NRL
9	Pentachlorodiphenyl	5.0[b]	1.67	0.0130	NRL (*19*)

[a] At 20° C. and audio frequency.

[b] At 25° C. and 1000 cps.

of uncertainties associated with prediction of dipole moment from structure, only a reasonable approximation is needed. The data may extrapolated from the refractive indexes and densities of related, known compounds or, if necessary, the refractive index may be calculated from the approximate atomic and bond refractions (35) and density.

Density may be calculated with sufficient accuracy from the parachor, taking into account the parachor for the C-F bond as reported by Murphy and others (*10*). This calculation involves surface tension, which often can be extrapolated by analogy from the surface tensions of known compounds listed by Quayle (*26*). Since the surface tension enters the parachor equation only to the ¼ power, an error of 1 dyne (4%) in surface tension will contribute only a 1% error to the calculated density.

The surface tension of new fluorine-substituted compounds may be estimated roughly from that of the unsubstituted parent compound and the percentage of fluorine substitution. The relation between percentage fluorine substitution and percentage reduction in surface tension in the case of noncyclic esters (*4, 11, 12, 26, 41*) is represented graphically in Figure 2. The presence of CF_3 terminal groups leads to a much greater decrease in surface tension than would occur if only $—CF_2—$ elements are present in the molecule. If the surface tension of the parent compound is above or below the range of 28 to 32 dynes which characterizes the esters of Figure 2, the percentage effect of fluorine substitution will be correspondingly greater or less.

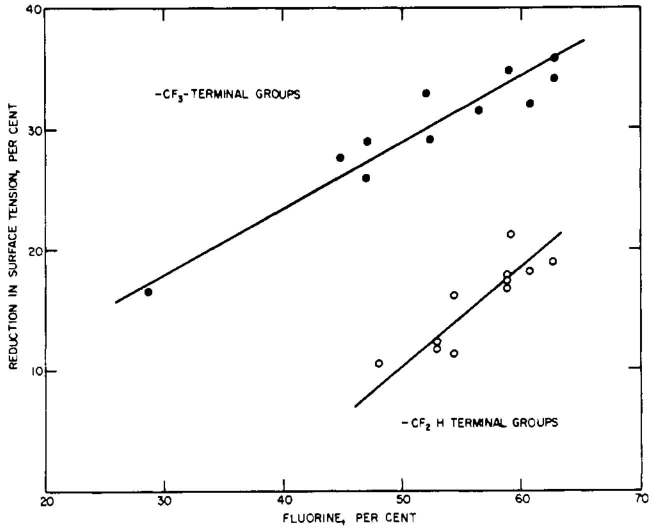


Figure 2. Relation of fluorine content to lowering of surface tension of noncyclic esters

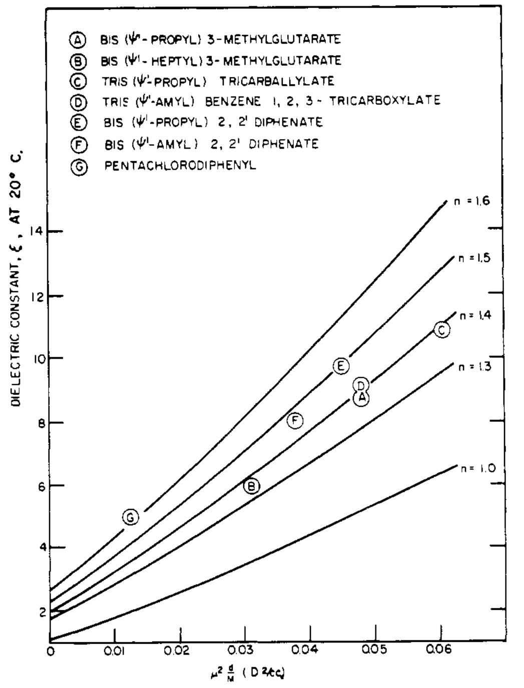


Figure 3. Relative contribution of orientation polarization and of electronic polarization to dielectric constant

Surface tension can also be estimated from the density and vapor pressure of a liquid by means of an equation given by Reich (*27*).

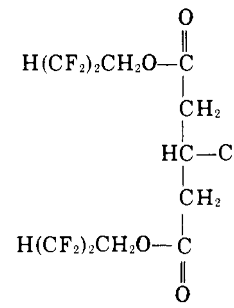
APPLICATION OF STRUCTURAL GUIDES TO PREPARATION OF NEW CAPACITOR IMPREGNANTS

With the foregoing principles in mind, a number of new, partially fluorinated esters have been synthesized by Murphy and others (*20*). The structures, names, and abbreviations of these compounds, several of which have not been reported, appear in Table IX. Pertinent physical and electrical properties are given in Table X.

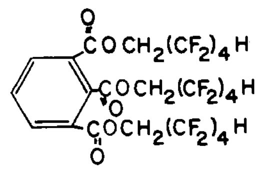
Relative contributions of dipole polarization and electronic polarization to the dielectric constants of the compounds listed in Table X may be estimated from Figure 3. The gain from electronic polarization is especially notable for pentachlorodiphenyl and for aromatic fluoroesters.

By referring to Table X, it is seen that of the new compounds synthesized, four stand out in terms of high dielectric constant—bis(ψ'-propyl) 3-methylglutarate, tris(ψ'-propyl) tricarballylate, tris(ψ'-amyl) 1,2,3-benzenetricarboxylate, and bis(ψ'-propyl) 2,2'-diphenate. The bis-

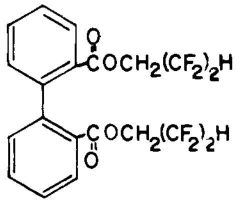
Table IX. Structures, Names, and Abbreviations of Fluorinated Esters (*10*)



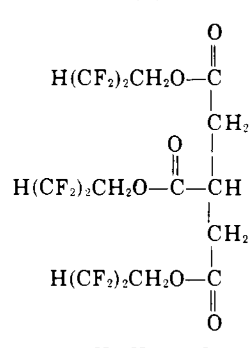
Bis(1*H*,1*H*,3*H*-tetrafluoropropyl) 3-methylglutarate
Bis(ψ'-propyl) 3-methylglutarate



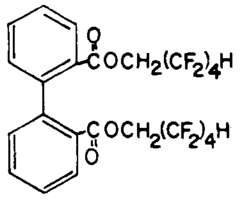
Tris(1*H*,1*H*,5*H*-octafluoropentyl) benzene 1,2,3-tricarboxylate
Tris(ψ'-amyl)benzene 1,2,3-tricarboxylate



Bis(1*H*,1*H*,3*H*-tetrafluoropropyl) 2,2'-diphenate
Bis(ψ'-propyl) 2,2'-diphenate



Tris(1*H*,1*H*,3*H*-tetrafluoropropyl) tricarballylate
Tris(ψ'-propyl) tricarballylate



Bis(1*H*,1*H*,5*H*-octafluoropentyl) 2,2'-diphenate
Bis(ψ'-amyl) 2,2'-diphenate

Table X. Properties of New High Dielectric Constant Liquids

Compound	Dielectric Constant, ε at 20° C., 60 Cps.	Molecular Weight, Theoretical	Density, G./Ml. at 20° C.	Index of Refraction n_D^{20}	Viscosity, Cs.		Boiling Point, ° C. per Mm. Hg	Flash Point, ° F.	Pour Point, ° F.
					68° F.	210° F.			
Bis(ψ'-propyl) 3-methylglutarate	8.85	374.23	1.4012	1.3791	22[c]	2.14	95/0.4	...	...
Tris(ψ'-propyl) tricarballylate	10.8	518.26	1.5514	1.3810	283.5	5.90	154/0.7	410	−30
Tris(ψ'-amyl)benzene 1,2,3-tricarboxylate	8.98	852.34	1.7030	1.3939	2800[f]	19.1	190/0.3	...	...
Bis(ψ'-propyl) 2,2'-diphenate	9.70	470.31	1.4342	1.4891	1190	8.47	168/1.3	425	0
Bis(ψ'-amyl) 2,2'-diphenate	8.0	670.35	1.5622	1.4469	1000[e]	10.3	175/0.5	430	−5
Bis(ψ'-heptyl) 3-methylglutarate[a]	6.1	774.31	1.6484	1.3503	66[e]	3.70	147/0.5	440	−30
Pentachlorodiphenyl[b]	5.0[c]	326	1.533[d]	1.64[d]	8600[e,g]	6[e,g]	365–390/760[h]	None	50[g]

[a] Compound studied in earlier work (*5*) for comparison.
[b] Typical commercial liquid dielectric (*19*) for comparison.
[c] At 25° C. and 1000 cps.
[d] At 25° C.
[e] Interpolated values
[f] Extrapolated
[g] Approximate.
[h] Distillation range.

(ψ'-amyl) 2,2'-diphenate, which was synthesized for lubricant use, is also of interest, because it is a stable liquid at higher temperatures than aliphatic fluoroesters (*20*). The introduction of smaller alcohol groups lowers the boiling points of the esters; this may place a restriction on the use of bis(ψ'-propyl)3-methylglutarate. The volatility of the four other compounds is as low or lower than that of bis(ψ'-heptyl)3-methylglutarate, which has been successfully used as a capacitor impregnant (*5*). A second limiting factor is behavior at low temperatures. Partially fluorinated esters tend to supercool instead of to crystallize (*10*), which extends the useful low-temperature range. It is possible that these new esters may give adequate low-temperature performance, although their viscosities are higher than that of the bis(ψ'-heptyl)3-methylglutarate.

Studies of the oxidation, thermal, and hydrolytic stability of these compounds are in progress. Data available indicate that the oxidation stabilities of both the bis(ψ'-propyl)-tricarballylate and bis(ψ'-propyl)2,2'-diphenate are better than that of the bis(ψ'-heptyl)3-methylglutarate studied previously. The stability of the bis(ψ'-amyl)2,2'-diphenate to oxidation, thermal decomposition, and hydrolysis is excellent (*20*).

The final choice of compounds for practical development will depend upon the weighting given to conflicting requirements of low volatility and low viscosity and upon the importance attached to dielectric constants in excess of 8.

ACKNOWLEDGMENT

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