Some Physical Properties of Long-Chained Esters of Dibasic Acids

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AN ANALYSIS of carnauba wax by dielectric spectroscopy (*1*) led to the synthesis of several waxlike materials.

The technique of dielectric spectroscopy is employed to investigate the behavior of materials in terms of their molecular and atomic constituents during analysis of their dielectric constants and losses. This technique establishes presence and magnitude of permanent electric moments in the component molecules, establishes whether association exists, and determines the degree of crystallinity of the material.

It has been found through such an analysis of carnauba wax, that the esters present are aligned in an orderly fashion in the solid state with strong head to head attractions between molecules and strong cohesion of parallel chains through hydrogen bonding. These esters are bidipolar in structure.

To find a material that would be a suitable substitute for carnauba wax in the making of carbon transfer inks, several new bidipolar esters were prepared. Three normal long-chain alcohols—dodecanol, octadecanol, and docosanol—were used. Each of these alcohols was reacted with a series of dibasic acids—succinic, glutaric, adipic, pimelic, azelaic, sebacic, and tetradecandioic—and resulted in the diesters. Monoesters were prepared from succinic and glutaric anhydrides (Table I).

EXPERIMENTAL

General Procedure for Diesters. To a 250-ml. round-bottomed flask fitted with a Dean-Stark water trap and an Allihn condenser was added a 1 to 2 molar ratio of dicarboxylic acid and alcohol. As a catalyst for this reaction 1 to 5%

Table I. Elemental Analysis

Esters	M.W.	Empirical Formula	Found, % C	Found, % H	Found, % O	Calculated, % C	Calculated, % H	Calculated, % O
Succinates								
Didodecyl	454.82	$C_{28}H_{54}O_4$	74.48	12.12	13.50	73.94	11.99	14.07
Dioctadecyl	623.18	$C_{40}H_{78}O_4$	77.50	12.82	10.40	77.09	12.64	10.27
Didocosyl	735.42	$C_{48}H_{94}O_4$	78.42	13.13	8.87	78.39	12.91	8.70
Monododecyl	286.46	$C_{16}H_{30}O_4$				67.08	10.58	22.34
Mono-octadecyl	370.64	$C_{22}H_{42}O_4$	71.51	11.41	17.42	71.42	11.45	17.27
Monodocosyl	426.76	$C_{26}H_{50}O_4$	73.29	11.98	14.79	73.17	11.83	15.00
Glutarates								
Didodecyl	468.85	$C_{29}H_{56}O_4$	74.32	12.16	13.60	74.29	12.06	13.65
Dioctadecyl	637.21	$C_{41}H_{80}O_4$	77.07	12.56	9.99	77.20	12.69	10.05
Didocosyl	749.45	$C_{49}H_{96}O_4$	78.56	12.94	8.60	78.51	12.93	8.55
Monododecyl	300.49	$C_{17}H_{32}O_4$				67.94	10.75	21.29
Mono-octadecyl	384.67	$C_{23}H_{44}O_4$	72.25	11.50	16.52	71.90	11.50	16.65
Monodocosyl	440.79	$C_{27}H_{52}O_4$	73.83	11.82	14.74	73.60	11.91	14.51
Adipates								
Didodecyl	482.88	$C_{30}H_{58}O_4$	74.56	11.86	13.28	74.61	12.13	13.25
Dioctadecyl	651.24	$C_{42}H_{82}O_4$	77.56	12.72	10.03	77.46	12.72	9.83
Didocosyl	763.48	$C_{50}H_{98}O_4$	78.67	13.10	8.37	78.65	12.96	8.38
Pimelates								
Didodecyl	496.91	$C_{31}H_{60}O_4$	75.17	12.18	13.09	74.92	12.20	12.88
Dioctadecyl	665.27	$C_{43}H_{84}O_4$	77.85	12.77	9.59	77.63	12.75	9.62
Didocosyl	777.51	$C_{51}H_{100}O_4$	78.81	13.20	8.37	78.78	12.99	8.23
Azelates								
Didodecyl	524.97	$C_{33}H_{64}O_4$	75.68	12.52	12.34	75.51	12.31	12.19
Dioctadecyl	693.33	$C_{45}H_{88}O_4$	77.71	12.64	9.87	77.94	12.81	9.23
Didocosyl	805.57	$C_{53}H_{104}O_4$	78.74	13.09	8.50	78.89	13.03	7.93
Sebacates								
Didodecyl	539.00	$C_{34}H_{66}O_4$	75.88	12.17	12.08	75.76	12.37	11.87
Dioctadecyl	707.36	$C_{46}H_{90}O_4$	78.38	12.93	9.22	78.10	12.85	9.05
Didocosyl	819.60	$C_{54}H_{106}O_4$	79.26	13.29	7.82	79.13	13.06	7.81
Tetradecanates								
Didodecyl	595.12	$C_{38}H_{74}O_4$	76.87	12.61	10.73	76.69	12.56	10.75
Dioctadecyl	763.48	$C_{50}H_{98}O_4$	78.91	12.80	8.60	78.65	12.96	8.38
Didocosyl	875.72	$C_{58}H_{114}O_4$	79.81	13.12	7.28	79.54	13.15	7.31

of a *p*-toluenesulfonic acid was added (based on weight of the dicarboxylic acid). A fivefold excess of toluene (based on weight of the alcohol) was used as a solvent. The mixture was then allowed to react with the azeotropic distillation of water. When an equivalent volume of water was collected in the Dean-Stark water trap, the reaction was stopped. The solvent (toluene) was then removed in vacuo. The residue was crystallized in a suitable solvent (Table II).

General Procedure for Monoesters. To a 250-ml. round-bottomed flask fitted with an Allihn condenser were added equal moles of acid anhydride and alcohol. A fivefold excess of toluene (based on weight of alcohol) was added as a solvent. The mixture was allowed to react for 5 hours. The solvent was then removed in vacuo, and the residue crystallized in a suitable solvent (Table II).

RESULTS AND DISCUSSION

The esters so prepared were all white, crystalline solids. Physical constants are tabulated in Table II. Both melting points and refractive indices increase with increasing alcohol chain length within a given series, but change very little when acid chain length is increased. Consequently, the melting points—for example, the esters of docosyl alcohols—are approximately the same.

Infrared spectra were obtained through the use of potassium bromide pellets and on a Perkin-Elmer Model 21 spectrophotometer. The ester carbonyl peak for the diesters (Figures 1 to 7) occurs between 1730 and 1738 cm.$^{-1}$; longer acids series occur at the latter measurement. The glutarates (Figure 2) show a major peak at 1738 cm.$^{-1}$ and a doublet

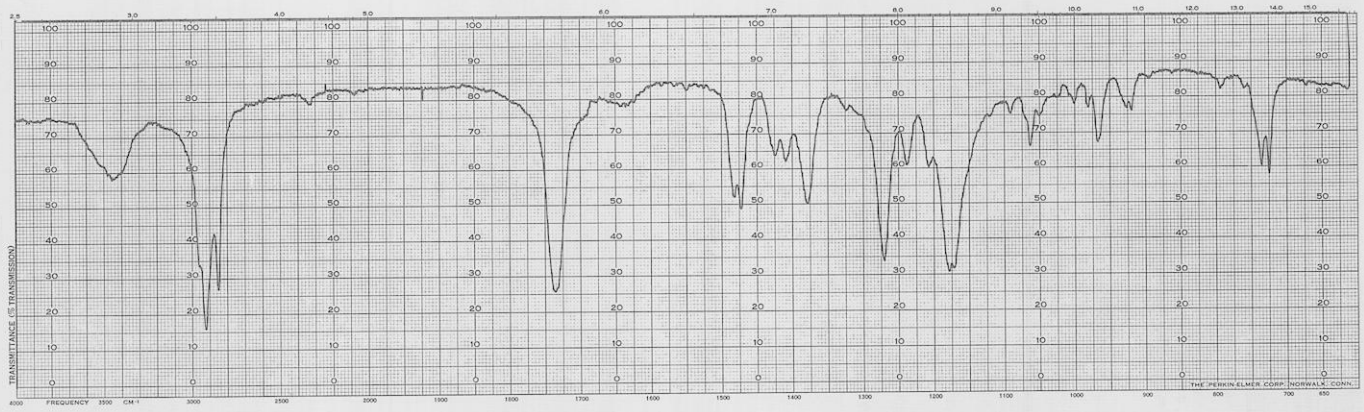

Figure 1. Infrared spectrum of dioctadecyl succinate

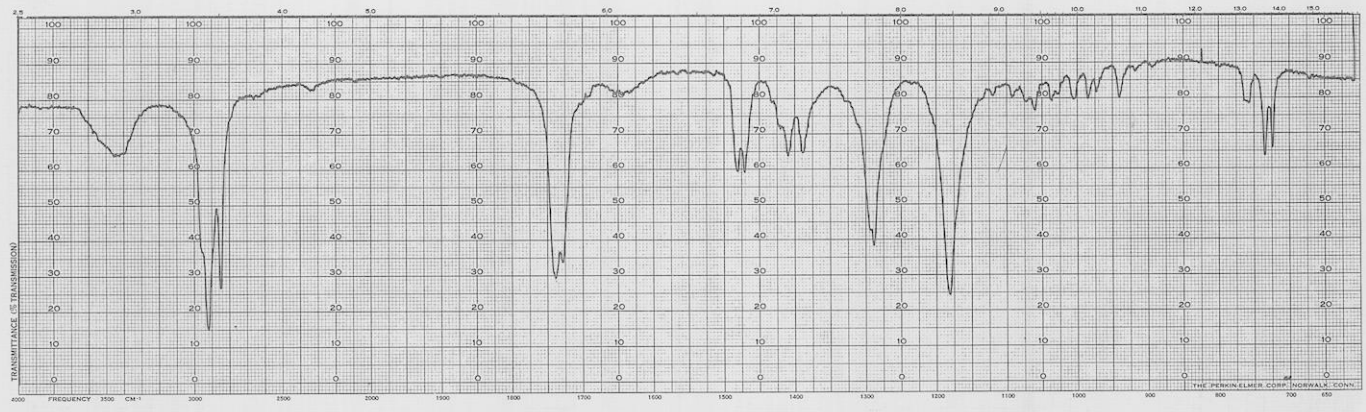

Figure 2. Infrared spectrum of dioctadecyl glutarate

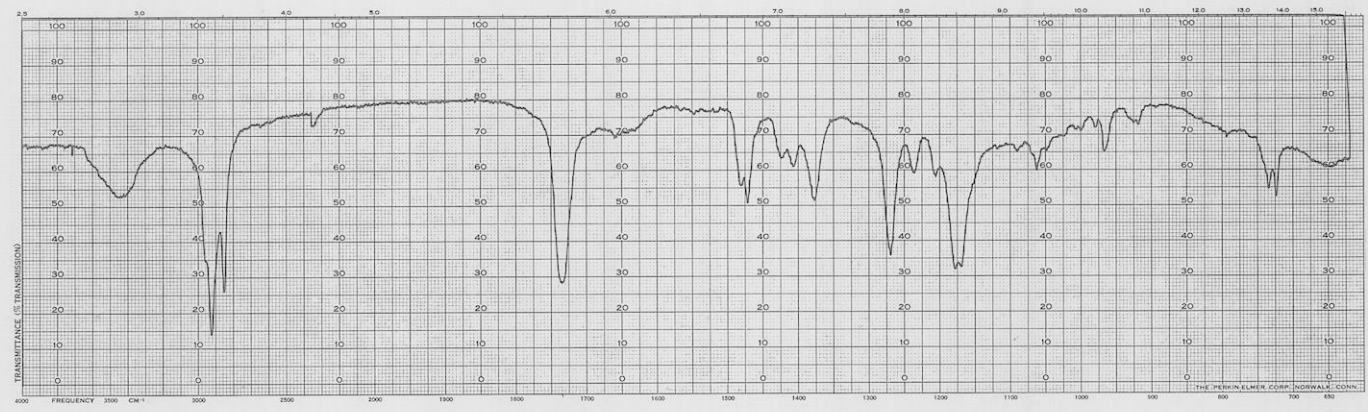

Figure 3. Infrared spectrum of dioctadecyl adipate

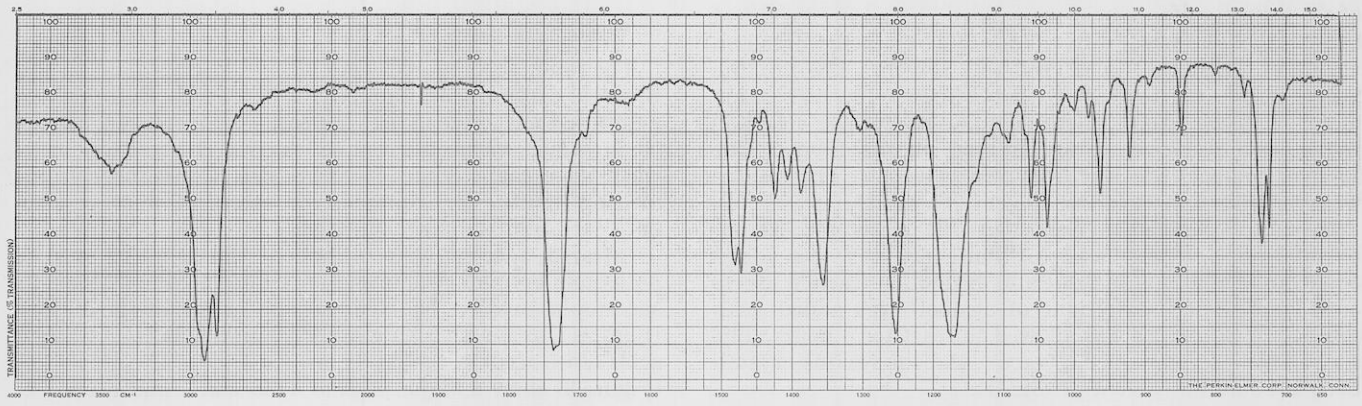

Figure 4. Infrared spectrum of dioctadecyl pimelate

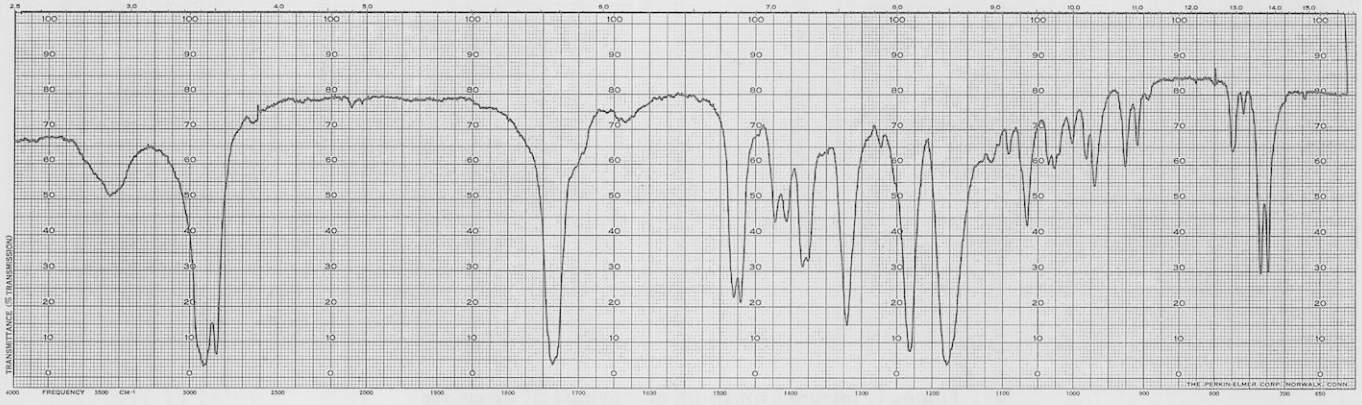

Figure 5. Infrared spectrum of dioctadecyl azelate

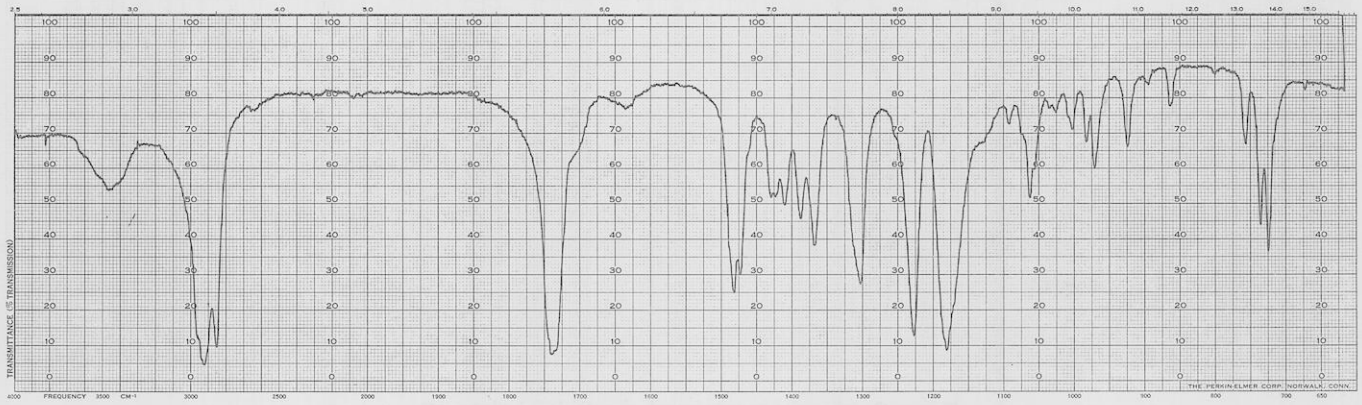

Figure 6. Infrared spectrum of dioctadecyl sebacate

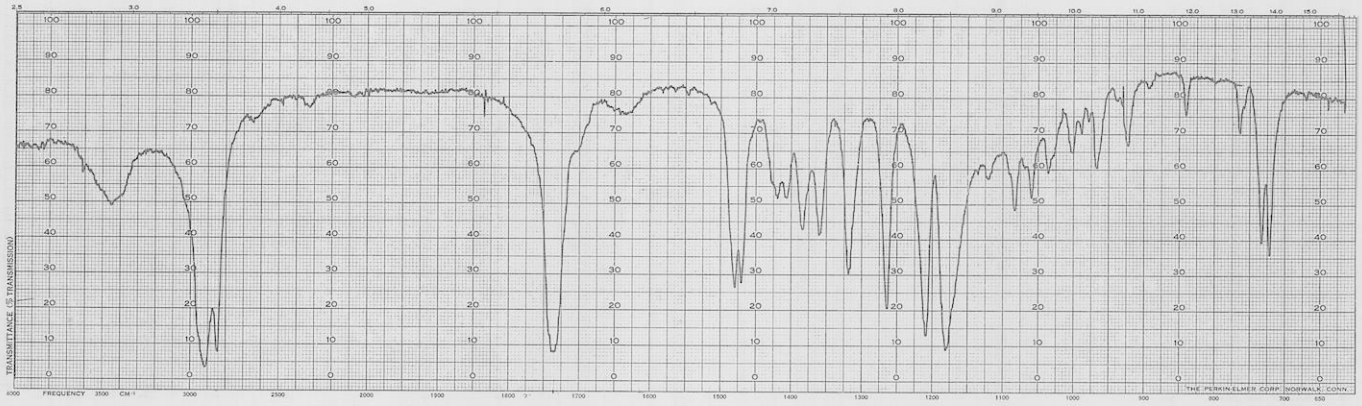

Figure 7. Infrared spectrum of dioctadecyl tetradecanate

Table II. Physical Constants

Esters	Index of Refraction (90° C.)	M.P., ° C.[a]	Recrystallization Solvents	Neutralization Equivalents	Yield, %
Succinates					
Didodecyl	1.4278	39.2–40.0	Methanol (5° C.)	...	48.4
Dioctadecyl	1.4351	67.2–68.0	THF/ethyl alcohol	...	82.5
Didocosyl	1.4382	79.5–80.1	THF	...	66.4
Monododecyl	1.4281	47.1–47.5	Distillation	289.22	24.2
Mono-octadecyl	1.4339	71.4–72.0	Ethyl acetate	356.10	57.8
Monododosyl	1.4361	80.3–81.0	THF/ethyl alcohol	427.99	65.0
Glutarates					
Didodecyl	1.4289	40.5–41.0	Methanol	...	21.6
Dioctadecyl	1.4356	65.5–66.0	Isopropyl alcohol	...	60.1
Didocosyl	1.4384	74.5–75.1	THF	...	22.5
Monododecyl	1.4330	60.0–62.0	Methanol (5° C.)	...	54.4
Mono-octadecyl	1.4350	74.5–75.0	Isopropyl alcohol	385.49	57.2
Monodocosyl	1.4365	82.5–83.0	THF/ethyl alcohol	433.85	59.5
Adipates					
Didodecyl	1.4289	40.0–40.6	Methanol	...	82.0
Dioctadecyl	1.4350	65.0–66.0	Isopropyl alcohol	...	74.4
Didocosyl	1.4386	73.5–74.0	THF	...	60.4
Pimelates					
Didodecyl	1.4318	41.5–42.0	Methanol (5° C.)	...	68.7
Dioctadecyl	1.4363	65.0–65.5	Ethyl alcohol	...	55.2
Didocosyl	1.4384	72.0–72.8	THF/methanol	...	55.4
Azelates					
Didodecyl	1.4318	41.0–41.5	Methanol	...	65.1
Dioctadecyl	1.4375	64.7–65.4	Isopropyl alcohol	...	61.4
Didocosyl	1.4395	73.0–73.4	THF	...	54.6
Sebacates					
Didodecyl	1.4319	48.7–49.2	Ethyl alcohol	...	46.9
Dioctadecyl	1.4372	65.1–65.7	THF	...	44.7
Didocosyl	1.4392	73.4–74.0	THF	...	63.8
Tetradecanates					
Didodecyl	1.4351	47.8–48.2	Methanol	...	52.6
Dioctadecyl	1.4388	71.3–71.6	THF/ethyl alcohol	...	70.7
Didocosyl	1.4395	74.6–75.4	THF/ethyl alcohol	...	67.4

[a] Melting points obtained by use of micro hot stage and are uncorrected.

Table III. Electrical Measurements

(Frequency = 100 kc.)

	Dielectric Constant at M.P.	Dielectric Loss at M.P.	Dielectric Constant (25° C.)	Dielectric Loss (25° C.)	Resistivity, Ohm-Cm.
Sebacates					
Didodecyl	3.59	0.000	2.64	0.019	2.57×10^{14}
Dioctadecyl	3.16	0.000	2.43	0.006	1.43×10^{14}
Didocosyl	2.84	0.006	2.34	0.000	3.86×10^{14}
Pimelates					
Didodecyl	3.56	0.000	2.50	0.000	9.15×10^{14}
Dioctadecyl	3.21	0.000	2.52	0.000	4.75×10^{14}
Didocosyl	3.04	0.000	2.37	0.000	1.31×10^{15}
Adipates					
Didodecyl	3.70	0.002	2.59	0.000	1.49×10^{13}
Dioctadecyl	3.22	0.000	2.47	0.000	9.15×10^{14}
Didocosyl	3.07	0.016	2.46	0.000	2.86×10^{14}
Glutarates					
Didodecyl	3.68	0.000	2.46	0.000	1.00×10^{14}
Dioctadecyl	3.08	0.020	2.43	0.000	1.24×10^{14}
Didocosyl	2.83	0.020	2.36	0.000	1.26×10^{14}

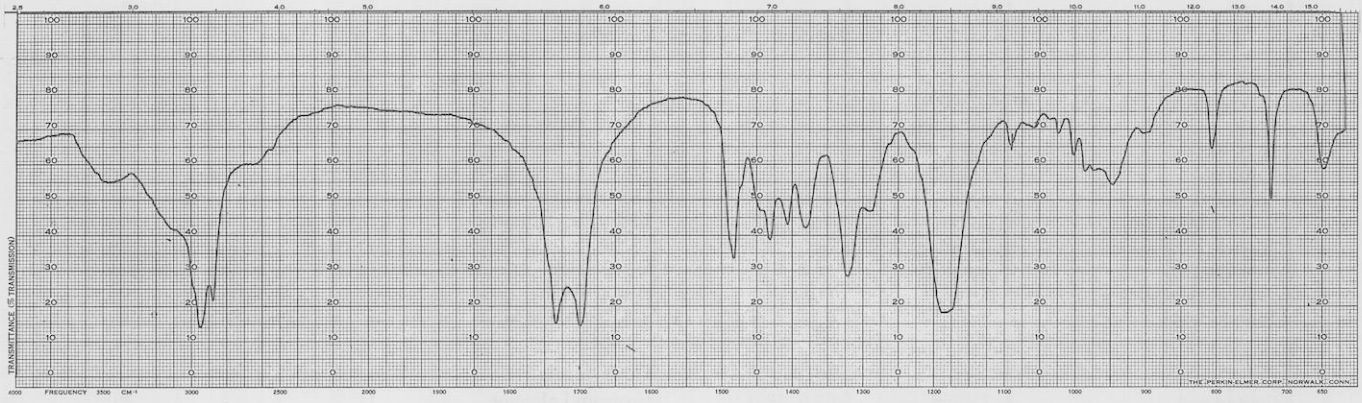

Figure 8. Infrared spectrum of mono-octadecyl succinate

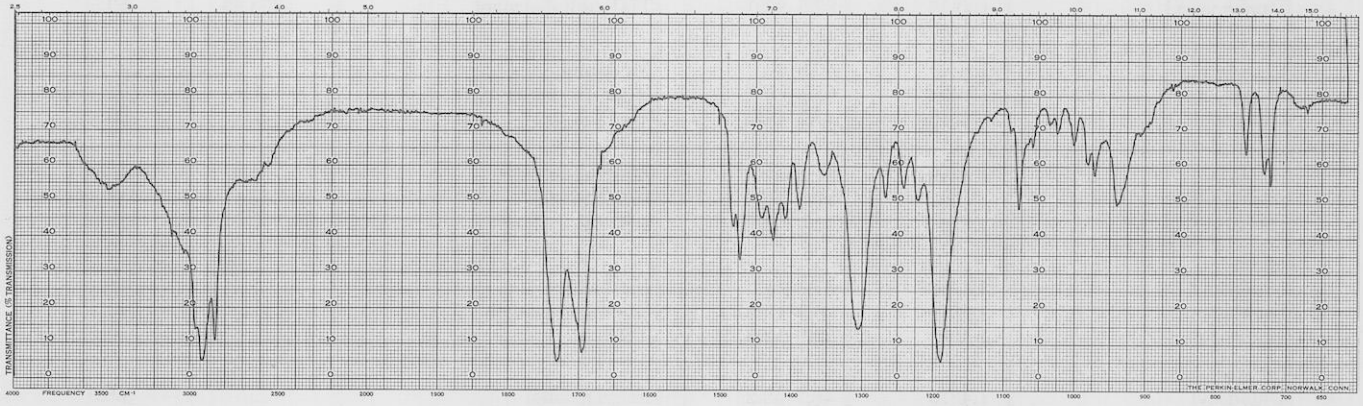

Figure 9. Infrared spectrum of mono-octadecyl glutarate

at 1728 cm.$^{-1}$ The spectra of the monoesters indicate the presence of twin carbonyl peaks. In the monosuccinate series (Figure 8) these peaks occur at 1700 and 1735 cm.$^{-1}$ The former is due to the absorption of the free acid carbonyl, and the latter to the ester carbonyl. These peaks are shifted slightly to 1695 and 1730 cm.$^{-1}$ in the monoglutarate series (Figure 9).

The capacitance and dissipation factor of the diesters of the adipate, glutarate, pimelate, and sebacate series were measured on a General Radio 1610-A capacitance bridge assembly using a two-terminal Elliott sample cell, modified so that dry nitrogen gas could be passed around the electrodes and sample to eliminate moisture condensation. Measurements were made at 25° C. and a frequency of 100 kc. The dielectric constant and loss factors were calculated on the basis of a paraffin calibration of the sample cell (Table III). The second and third columns show the dielectric constants and loss factors at the temperature just prior to melting and the fourth and fifth columns show the same values at 25° C. In each case the dielectric constant increases with decreasing length of the alcohol portion and tends to increase with decreasing length of the acid portion within both the even and odd series. However, the effect of the length of the acid chain in the molecular structure must also be taken into account.

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