bromide have been made from liquid nitrogen temperatures to temperatures well above their melting points in a heat conduction type calorimeter, so constructed that the calorimeter can serve also as a dielectric cell. *t*-Butyl chloride and *t*-butyl bromide, because of their spherical shape, have marked rotational transitions above which their molecules can orient freely in the lattice. *i*-Propyl bromide showed less rise in dielectric constant below the melting point than had previously been observed. *n*-Amyl bromide showed the existence of two solid forms, one of which is unstable. By rapid cooling, the unstable or lower melting form could be obtained at liquid nitrogen temperatures. Subsequent warming indicated an optimum temperature at which this form changed spontaneously into the higher melting more stable form. The heat capacity of both forms has been measured.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Thermal and Dielectric Evidence of Polymorphism in Some Long-Chain *n*-Alkyl Bromides[1]

BY ROBERT W. CROWE AND CHARLES P. SMYTH

It has been realized for some time that many straight-chain organic compounds are capable of existing in more than one form in the solid state, the particular modification assumed being dependent not only upon the substance itself but upon its previous history and to a large extent upon its present environment. This phenomenon has been studied in long-chain acids,[2,3,4,5] esters,[4,6] alcohols,[4,6,7,8] halides,[5,9] hydrocarbons[10] and other compounds by cooling curves, X-ray studies and dielectric constant measurements. In many cases the transitions from one form to another are monotropic and appear only on cooling, especially in the shorter members of the series. These changes are usually attributed to changes in the angle of tilt of the hydrocarbon chain with respect to the terminal plane in the crystal. Dielectric constant studies have shown the possibility of molecular rotation about the long axis in some forms. Polymorphism, however, is not common in members of an homologous series until the number of carbon atoms in the chain exceeds thirteen or fourteen with the result that very few studies have been made on the lower members. Thermal measurements by Deese,[11] dielectric studies by Baker and Smyth,[12] and more recent thermal and dielectric measurements in this Laboratory[13] on *n*-amyl bromide have shown, however, that this compound exists in two solid modifications with different melting points, the lower melting form being the less stable. Mair[14] has also been able to isolate two forms of *n*-nonyl bromide with melting points −29.06 and −30.71°. It has seemed desirable to investigate dielectrically and thermally a number of the lower bromides in an effort to determine whether polymorphism is a characteristic only of the odd members and whether rotational freedom about the long axis exists in any of the forms.

In this investigation, simultaneous dielectric constant and heat capacity measurements were made on *n*-heptyl, *n*-octyl, *n*-nonyl and *n*-undecyl bromides from liquid nitrogen temperatures to temperatures above their respective melting points. In addition, dielectric constant measurements were made on these compounds as well as on *n*-decyl, *n*-tridecyl and *n*-pentadecyl bromides in the vicinity of their melting points with a much lower rate of change of temperature.

Purification of Materials

n-Heptyl bromide from the Paragon Testing

TABLE I

MELTING POINTS AND REFRACTIVE INDICES OF BROMIDES

No. of C atoms	This research M. p., °C.	This research n^{20}_D	Literature M. p., °C.	Literature n^{20}_D
7	−58.8 and −56.1	1.45057	−58.86,[15] −58.25[16]	1.45052[17]
8	−55.0	1.45267	−55.0[18]	1.45267[17], 1.4527[19]
9	−30.8 and −29.0	1.45467	−30.84[4] −30.71 and −29.06[14]	1.45417[17]
10	−29.2	1.45607	−29.62[4]	1.45527[17], 1.4558[19]
11	− 9.9	1.45777	−13.15[4]	1.45697[17]
13	5.9		5.94[4]	
15	18.5		18.63[4]	

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(1) This research was carried out with the support of the Office of Naval Research.

(2) Garner and King, *J. Chem. Soc.*, 1849 (1929).

(3) Francis, Piper and Malkin, *Proc. Roy. Soc.* (*London*), **A128**, 214 (1930).

(4) Meyer and Reid, THIS JOURNAL, **55**, 1574 (1933).

(5) Francis, Collins and Piper, *Proc. Roy. Soc.* (*London*), **A158**, 691 (1937).

(6) Baker and Smyth, THIS JOURNAL, **60**, 1229 (1938).

(7) Hoffman and Smyth, *ibid.*, **71**, 431 (1949).

(8) Ott, *Z. physik. Chem.*, **193**, 218 (1944).

(9) Hoffman and Smyth, to be published.

(10) Muller, *Proc. Roy. Soc.* (*London*), **A138**, 514 (1932).

(11) Deese, THIS JOURNAL, **53**, 3673 (1931).

(12) Baker and Smyth, *ibid.*, **61**, 1695 (1939).

(13) Kushner, Crowe and Smyth, *ibid.*, **72**, 1091 (1950).

(14) Mair, *Bur. Standards J. Research*, **9**, 457 (1932).

(15) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1947.

(16) Sherrill, THIS JOURNAL, **52**, 1982 (1930).

(17) Vogel, *J. Chem. Soc.*, 636 (1943).

(18) Deffet, *Bull. soc. chim. Belg.*, **40**, 385 (1931).

(19) Whitmore, Sutherland and Cosby, THIS JOURNAL, **64**, 1360 (1942).

Laboratories, *n*-octyl bromide and *n*-decyl bromide from Halogen Chemicals, Inc., and *n*-undecyl bromide from Columbia Organic Chemicals Co., Inc., were purified by fractional distillation under reduced pressure in a five-foot column packed with glass helices, and the best fractions collected. *n*-Nonyl, *n*-tridecyl and *n*-pentadecyl bromides were kindly given to us already purified by Dr. E. Emmet Reid. These compounds were used as received without further purification. The melting points and refractive indices of the compounds investigated are compared with the literature values in Table I.

Experimental Method and Results

The simultaneous heat capacity and dielectric constant measurements were made with the combined heat conduction calorimeter and dielectric cell previously described.[18] An impedance bridge[7,20] was used in conjunction with this apparatus for determining the dielectric constants. It is estimated that the average error in measurement of the heat capacity is ±0.5 cal./deg. mole. The dielectric constants obtained with the calorimeter cell had a probable error of ±1%. The average rate of warming during these measurements was about 0.5° per minute.

Another cell, also previously described,[7] was used for determining the dielectric constants of the compounds at the low rate of temperature change. The average rate of cooling and warming for these measurements was about 0.1° per minute, and the time required for melting and freezing was about one hour. The average error in dielectric constant using this cell was about ±1%. Each compound was run several times, and the data presented here represent the most reproducible runs on the purest samples.

The heat capacities (cal./deg. mole) and dielectric constants of *n*-heptyl, *n*-octyl, *n*-nonyl and *n*-undecyl bromides are listed in Table II with the temperatures of measurement. In Table III are listed the dielectric constants of the compounds investigated, measured in the vicinity of their melting points. Since no frequency dependence was observed, dielectric constant values are reported only at 50 kc. The heats of

TABLE II

MOLAR HEAT CAPACITIES AND DIELECTRIC CONSTANTS OF *n*-HEPTYL, *n*-OCTYL, *n*-NONYL AND *n*-UNDECYL BROMIDES

t, °C.	C_p	ϵ'	*t*, °C.	C_p	ϵ'	*t*, °C.	C_p	ϵ'
n-Heptyl Bromide (metastable form)								
−160.5	26.4	2.38	−122.5	31.6		−93.5	37.8	
−156.0	27.0		−118.5	32.5	2.39	−90.0	38.1	
−151.0	27.3		−115.5	35.1		−86.5	38.9	
−147.5	27.7		−111.5	38.2		−83.0	39.6	
−143.0	28.3		−108.0	41.7	2.40	−80.0	35.9	2.44
−139.0	29.1		−104.0	52.9	2.42	−76.5	14.7	
−135.0	29.6		−100.5	52.7	2.43	−72.8		2.43
−131.0	30.3		−97.0	40.4	2.44	−70.0		2.40
−126.5	31.0							
(Stable form)								
−160.5	24.7	2.35	−108.0	31.7		−66.5	38.6	2.43
−156.0	25.3		−104.0	32.4		−63.5	40.7	2.44
−151.0	25.9		−100.5	33.0		−57.6		2.87
−147.5	26.3		− 97.0	33.4		−57.3		3.69
−143.0	26.9	2.36	− 93.5	33.8	2.39	−57.0		4.70
−139.0	27.4		− 90.0	34.4		−56.7		5.52
−135.0	28.0	2.37	− 86.5	34.8		−56.4		5.80
−131.0	28.6		− 83.0	35.3	2.40	−54.9		7.00
−126.5	29.3		− 80.0	35.7		−51.0	46.7	6.92
−122.5	29.7		− 76.5	36.0	2.41	−48.0	47.0	6.84
−118.5	30.1		− 73.0	36.6		−45.0	47.1	
−115.5	30.6		− 70.0	37.5	2.42	−42.0	47.1	6.71
−111.5	31.3	2.38						
n-Octyl Bromide								
−160.5	27.9	2.38	−111.5	35.3		−70.0	41.2	2.41
−156.0	28.7		−108.0	35.7		−66.5	42.0	
−151.0	29.0		−104.0	35.8		−63.5	42.7	
−147.5	29.8		−100.5	36.6		−60.0	47.4	2.43
−143.0	30.1		− 97.0	37.0		−56.7		2.50
−139.0	30.7		− 93.5	37.5		−55.7		4.35
−135.0	31.1		− 90.0	38.0		−55.2		5.65
−131.0	31.8		− 86.5	38.5		−53.0		6.41
−126.5	32.6		− 83.0	38.8		−51.0	62.4	6.37
−122.5	33.2		− 80.0	39.3	2.40	−42.0	62.3	6.29
−118.5	33.9	2.39	− 76.5	40.1		−39.0	62.3	6.15
−115.5	34.5		− 73.0	40.7				
n-Nonyl Bromide (metastable form)								
−160.5	32.6	2.36	−111.5	43.7	2.39	−70.0	46.5	2.45
−156.0	32.8		−108.0	47.3		−66.5	46.7	
−151.0	33.2		−104.0	53.2		−63.5	47.6	2.46
−147.5	33.7		−100.5	60.7	2.40	−60.0	47.8	
−143.0	34.0		− 97.0	53.3	2.42	−57.0	48.0	2.47
−139.0	34.1		− 93.5	47.6	2.43	−54.0	48.5	
−135.0	35.1		− 90.0	44.0		−51.0	49.4	2.48
−131.0	35.9		− 86.5	44.2		−48.0	50.5	
−126.5	36.8	2.37	− 83.0	44.4		−45.0	23.5	2.49
−122.5	37.8		− 80.0	44.7		−42.8		2.50
−118.5	39.2	2.38	− 76.5	45.2	2.44	−39.8		2.49
−115.5	41.0		− 73.0	45.9				
(Stable form)								
−160.5	31.9	2.35	−100.5	39.5		−51.0	46.6	
−156.0	32.2		− 97.0	40.0		−48.0	47.9	2.45
−151.0	33.2		− 93.5	39.8	2.40	−45.0	49.8	
−147.5	33.0		− 90.0	40.5		−42.0	51.7	2.46
−143.0	33.4	2.36	− 86.5	40.9		−39.0	57.1	2.48
−139.0	33.4		− 83.0	41.0		−36.0	74.4	2.49
−135.0	33.8		− 80.0	41.5	2.41	−31.6		2.67
−131.0	34.9		− 76.5	42.0		−30.2		4.26
−126.5	35.4	2.37	− 73.0	42.7		−29.5		4.97
−122.5	35.9		− 70.0	43.0	2.42	−28.3		5.53
−118.5	36.6		− 66.5	43.2		−24.5	68.8	5.48
−115.5	37.3		− 63.5	44.0	2.43	−21.5	68.9	5.44
−111.5	38.1	2.38	− 60.0	44.6	2.43	−18.5	68.5	5.40
−108.0	38.5		− 57.0	45.1	2.44	−16.0	68.5	5.37
−104.0	39.3	2.39	− 54.0	46.1				
n-Undecyl Bromide								
−151.0	37.6	2.32	− 90.0	76.3		−39.0	56.9	2.41
−147.5	38.0		− 86.5	71.4	2.36	−36.0	58.1	
−143.0	38.9		− 83.0	57.1	2.37	−33.0	59.4	2.42
−139.0	39.4		− 80.0	51.3		−30.0	60.3	
−135.0	39.7		− 76.5	49.8		−27.5	61.1	2.43
−131.0	40.7		− 73.0	50.2	2.37	−24.5	61.7	
−126.5	41.7	2.33	− 70.0	50.9		−21.5	68.6	2.44
−122.5	42.3		− 66.5	51.2		−18.5	72.2	2.45
−118.5	43.2		− 63.5	52.1		−16.0	78.7	2.46
−115.5	43.7		− 60.0	52.8		−11.9		2.57
−111.5	44.6		− 57.0	53.0	2.38	−10.5		3.42
−108.0	45.4		− 54.0	53.6		−10.0		3.87
−104.0	48.0		− 51.0	54.4	2.39	− 9.3		4.74
−100.5	51.2		− 48.0	54.9		− 3.3		4.63
− 97.0	55.7		− 45.0	55.5	2.40	− 0.6		4.61
− 93.5	62.8	2.34	− 42.0	55.7				

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[20] Smyth and Hitchock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).

TABLE III

DIELECTRIC CONSTANTS OF BROMIDES NEAR MELTING POINTS

t, °C.	ε'	t, °C.	ε'	t, °C.	ε'
n-Heptyl Bromide (cooling)					
−54.6	6.97	−59.1	3.30	−60.9	2.64
−57.3	7.04	−59.2	3.03	−61.4	2.60
−57.9	7.06	−59.4	2.91	−62.2	2.55
−59.7	7.08	−59.7	2.79	−62.9	2.53
−59.2	6.89	−60.0	2.73	−64.8	2.50
−59.1	6.77	−60.4	2.69		
(Warming immediately)					
−61.9	2.57	−59.2	2.91	−58.8	4.04
−60.7	2.64	−59.1	2.99	−58.7	7.06
−60.2	2.69	−59.0	3.17	−57.6	7.03
−59.4	2.82	−58.9	3.47	−56.6	7.01
(Warming after 18 hr. at −196°)					
−64.8	2.40	−57.6	2.51	−56.4	3.09
−61.9	2.41	−57.2	2.57	−56.3	3.35
−60.9	2.42	−57.0	2.63	−56.2	3.86
−59.4	2.43	−56.8	2.71	−56.1	5.85
−59.0	2.44	−56.7	2.77	−56.0	7.00
−58.5	2.46	−56.6	2.86	−55.7	6.96
−58.0	2.48	−56.5	2.97	−54.2	6.93
n-Octyl Bromide (cooling)					
−52.3	6.39	−55.3	4.79	−56.5	2.61
−55.8	6.47	−55.3	3.49	−57.4	2.51
−56.6	6.48	−55.4	3.07	−58.0	2.47
−55.6	6.21	−55.5	2.85	−58.8	2.44
−55.5	5.79	−55.8	2.72	−59.8	2.42
−55.4	5.31	−56.1	2.66	−60.8	2.41
(Warming)					
−61.9	2.40	−56.1	2.58	−55.1	4.05
−60.0	2.41	−55.9	2.63	−55.0	5.30
−59.0	2.43	−55.6	2.77	−55.0	6.05
−58.5	2.44	−55.5	2.96	−54.9	6.41
−57.6	2.47	−55.3	3.28	−54.6	6.40
−57.1	2.48	−55.2	3.55	−54.2	6.38
−56.6	2.52				
n-Nonyl Bromide (cooling)					
−19.7	5.36	−31.2	3.20	−33.5	2.62
−24.3	5.46	−31.3	3.05	−35.0	2.54
−29.0	5.54	−31.6	2.87	−35.9	2.52
−31.6	5.57	−32.0	2.77	−36.9	2.50
−31.3	5.46	−32.3	2.72	−38.0	2.48
−31.2	5.30	−33.0	2.65		
(Warming immediately)					
−36.4	2.50	−31.6	2.77	−30.9	3.61
−35.4	2.52	−31.4	2.87	−30.8	4.10
−34.4	2.55	−31.3	2.96	−30.7	4.80
−34.0	2.58	−31.2	3.09	−30.6	5.52
−32.5	2.69	−31.0	3.37	−28.2	5.51
−32.0	2.72				
(Warming after 18 hr. at −196°)					
−38.8	2.41	−30.1	2.58	−29.2	3.19
−36.9	2.41	−29.7	2.64	−29.1	3.52
−35.0	2.42	−29.5	2.75	−29.0	4.14
−33.0	2.44	−29.4	2.85	−29.0	5.53
−31.0	2.48	−29.3	2.98	−27.7	5.50
−30.6	2.51				
n-Decyl Bromide (cooling)					
−20.5	5.10	−29.9	5.03	−29.8	2.42
−23.5	5.15	−29.6	4.90	−30.2	2.38
−27.6	5.21	−29.5	4.80	−30.6	2.35
−29.7	5.25	−29.5	3.09	−31.7	2.32
−31.0	5.16	−29.6	2.50	−35.9	2.30
−30.4	5.09				
(Warming)					
−36.9	2.30	−30.4	2.39	−29.3	3.05
−33.0	2.32	−30.0	2.43	−29.2	4.17
−31.6	2.33	−29.5	2.55	−29.1	5.22
−31.1	2.35	−29.4	2.68	−28.7	5.21
n-Undecyl Bromide (cooling)					
− 6.3	4.68	−10.2	4.52	−10.8	2.57
− 8.3	4.70	−10.1	4.25	−11.8	2.51
− 9.3	4.72	−10.1	3.36	−12.7	2.47
−11.0	4.75	−10.2	2.68	−13.7	2.44
−10.6	4.66	−10.3	2.61	−14.7	2.42
−10.3	4.60	−10.5	2.59	−15.7	2.41
(Warming immediately)					
−16.7	2.41	−10.9	2.57	−10.1	2.97
−15.2	2.42	−10.7	2.60	−10.0	3.28
−13.2	2.45	−10.4	2.64	− 9.9	4.34
−12.2	2.48	−10.3	2.70	− 9.9	4.73
−11.3	2.53	−10.2	2.80	− 9.0	4.71
(Warming after 18 hr. at −196°)					
−14.7	2.40	−10.4	2.52	−10.0	2.96
−12.7	2.42	−10.3	2.55	− 9.9	3.74
−11.8	2.44	−10.2	2.60	− 9.9	4.44
−11.0	2.49	−10.1	2.71	− 6.8	4.71
n-Tridecyl Bromide (cooling)					
12.7	4.18	5.3	3.88	2.7	2.40
8.8	4.21	5.3	3.32	1.0	2.37
6.1	4.24	5.2	2.70	− 0.5	2.35
4.6	4.27	5.1	2.56	− 3.3	2.33
5.2	4.06	4.7	2.51		
(Warming immediately)					
− 4.9	2.32	4.9	2.53	5.7	2.77
− 2.9	2.33	5.0	2.55	5.8	2.95
1.0	2.36	5.1	2.54	5.9	3.28
3.0	2.39	5.2	2.54	6.0	4.05
4.0	2.43	5.4	2.58	6.1	4.20
4.5	2.46	5.5	2.61	8.0	4.19
4.6	2.49	5.6	2.68		
(Warming after 18 hr. at −196°)					
− 5.7	2.25	4.9	2.42	6.0	3.98
1.0	2.26	5.6	2.70	6.1	4.22
2.0	2.27	5.7	2.85	6.3	4.21
3.0	2.29	5.8	3.10	6.9	4.20
4.0	2.33	5.9	3.54		
n-Pentadecyl Bromide (cooling)					
20.2	3.88	17.9	3.25	16.2	2.46
18.9	3.90	17.8	2.79	15.2	2.42
17.4	3.91	17.7	2.69	14.2	2.39
17.7	3.87	17.6	2.59	13.2	2.37
17.8	3.82	16.9	2.50	10.3	2.35
17.9	3.76				

TABLE III (*Continued*)

t, °C.	ϵ'	t, °C.	ϵ'	t, °C.	ϵ'
(Warming immediately)					
10.8	2.34	17.5	2.54	18.4	3.01
12.8	2.36	17.7	2.54	18.5	3.41
13.7	2.37	17.9	2.58	18.6	3.69
15.7	2.42	18.0	2.61	18.7	3.84
16.6	2.48	18.2	2.72	19.1	3.88
17.3	2.53	18.3	2.85	19.6	3.87
(Warming after 18 hr. at −196°)					
10.8	2.31	17.1	2.46	18.4	3.23
13.7	2.32	17.5	2.51	18.5	3.54
14.7	2.34	18.1	2.67	18.6	3.76
15.7	2.36	18.2	2.81	18.7	3.87
16.2	2.38	18.3	2.95	19.8	3.87
16.6	2.40				

transition and fusion, as estimated here, are listed in Table IV.

TABLE IV

HEATS (APPARENT) OF TRANSITION AND HEATS OF FUSION OF BROMIDES

Bromide	ΔH_t (kcal./mole)	ΔH_f (kcal./mole)
n-Heptyl	0.20	5.2
n-Octyl		5.9
n-Nonyl	.19	7.2
n-Undecyl	.27	8.0

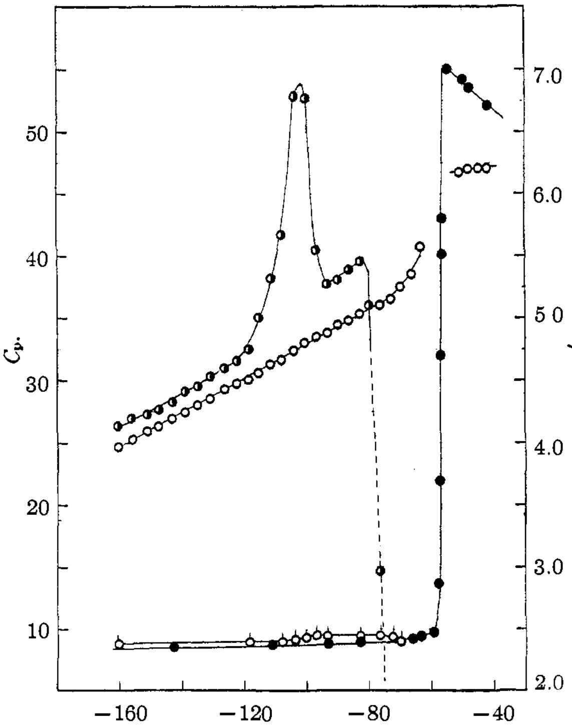

Fig. 1.—Temperature dependence of the dielectric constant and heat capacity of n-heptyl bromide. Filled circles and hollow circles represent dielectric constants and heat capacities, respectively, of the stable modification. Circles with tails and half-filled circles represent those of the metastable modification.

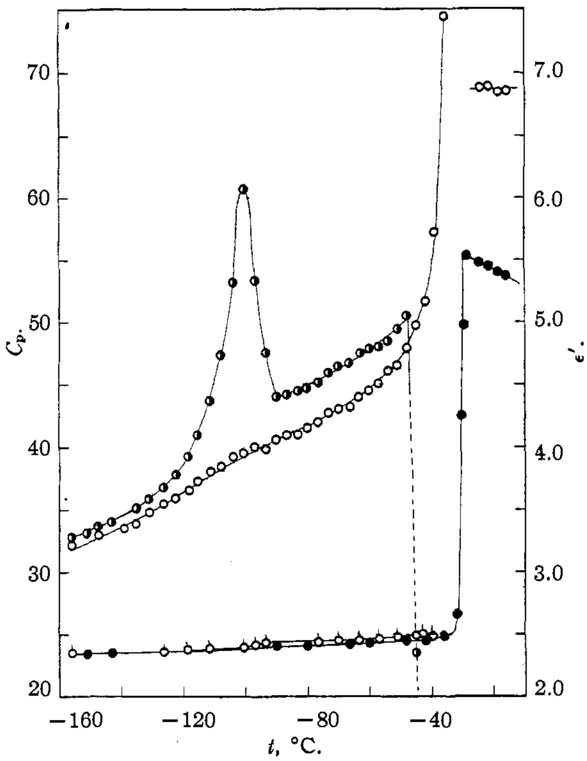

Fig. 2.—Temperature dependence of the dielectric constant and heat capacity of n-nonyl bromide. Filled circles and hollow circles represent dielectric constants and heat capacities, respectively, of the stable modification. Circles with tails and half-filled circles represent those of the metastable modification.

Discussion of Results

The heat capacity and dielectric constant curves for n-heptyl bromide and n-nonyl bromide in Figs. 1 and 2 clearly show that both of these compounds exist in two solid forms, the metastable form crystallizing from the liquid in each case. This form changes to the stable form on warming at temperatures several degrees below the melting point. This phenomenon has been observed previously in this Laboratory for n-amyl bromide.[13] Since heat is evolved in this change in crystal structure, the heat capacity values tend to become negative, as indicated by the dotted lines. In both compounds, small, reproducible lambda points appear in the metastable forms at temperatures below the point where the heat capacity drops sharply. Evidence of a similar transition was also found in n-amyl bromide, but, in this compound, the spontaneous change to the stable form took place before the transition was complete, making it impossible to estimate the heat involved. In the case of n-heptyl bromide, however, the transition appeared about 23° below this temperature and in n-nonyl bromide about 55° below. In order to measure the heat capacity of the stable crystals of these two compounds, the temperature was held constant at about 10° below the melting point for about one hour after the drop in heat capacity occurred. This technique ensured the complete disappearance of the metastable form. The compounds were then cooled again to liquid nitrogen temperatures and the runs repeated. The dielectric constants of the metastable forms are slightly higher than those of the stable forms but, as in the case of *n*-amyl bromide, not enough higher to indicate much orientational freedom in the crystals. The change in dielectric constant at the transitions in the metastable modifications is so slight as to indicate no appreciable change in molecular freedom.

In Figs. 3 and 4 are plotted the dielectric constants of *n*-heptyl bromide and *n*-nonyl bromide as functions of increasing and decreasing temperature in the vicinity of their melting points. Even though cooled very slowly, both compounds froze into the metastable form with relatively little supercooling. When they were warmed again within two or three hours of their freezing and without cooling more than 10° below their melting points, the resulting dielectric constants were practically identical with those obtained with decreasing temperature. Evidently, no appreciable change had occurred in the solid in that length of time. A small amount of hysteresis (about 0.3°) occurred in all measurements with this cell. However, when the temperature was decreased to about −190°, and the samples then allowed to warm, the dielectric constants were found to be somewhat lower and more nearly constant with temperature below the melting points. Also, the melting points were significantly higher for both substances. It should be noted that the dielectric constants of the lower melting forms continue to decrease quite rapidly with decreasing temperature for several degrees below the freezing point. This may be due to occasional molecular orientation about the long axis of the molecules in this region, which should occur more readily in the less tightly packed lattice of the metastable state.

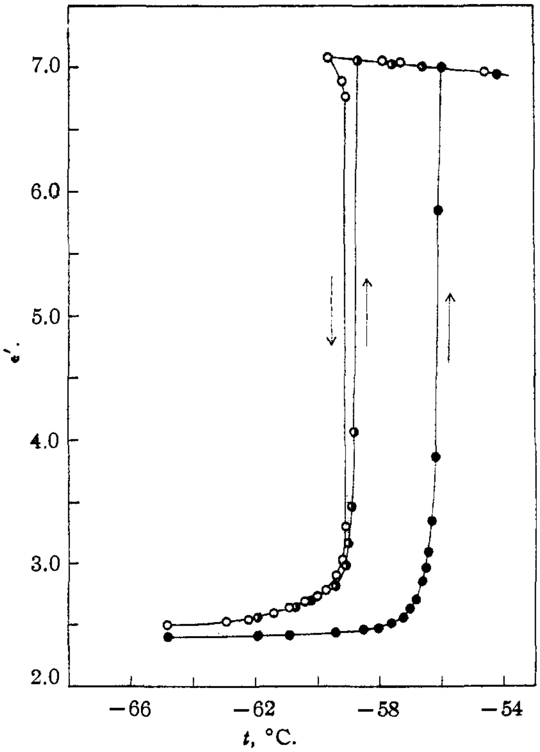

Fig. 3.—Temperature dependence of the dielectric constant of *n*-heptyl bromide near its melting point. Hollow circles are for cooling, half-filled circles for warming immediately after solidification, and filled circles for warming after eighteen hours at −196°.

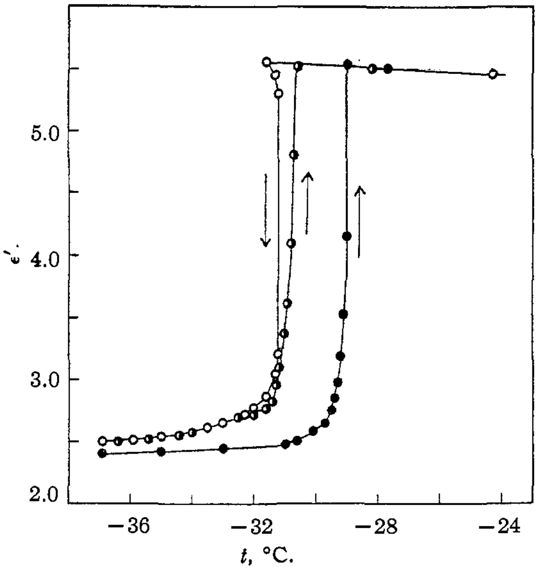

Fig. 4.—Temperature dependence of the dielectric constant of *n*-nonyl bromide near its melting point. Hollow circles are for cooling, half-filled circles for warming immediately after solidification, and filled circles for warming after eighteen hours at −196°.

An examination of the heat capacity and dielectric constant data for *n*-undecyl bromide (Figs. 5 and 6) shows that this compound also freezes into the lower melting form with little supercooling. The lambda point in the heat capacity curve is even more pronounced in this compound. The most striking difference between this and the other odd members investigated is the apparent stability of the metastable form. Even though held at liquid nitrogen temperatures for twenty-four hours, the compound showed no tendency to change to the higher melting form. Here again a very small increase in dielectric constant appeared at the transition point, and also in the region just below the melting point. It is entirely possible that the higher melting form could be isolated if the substance were held at low temperatures for a very long time. The

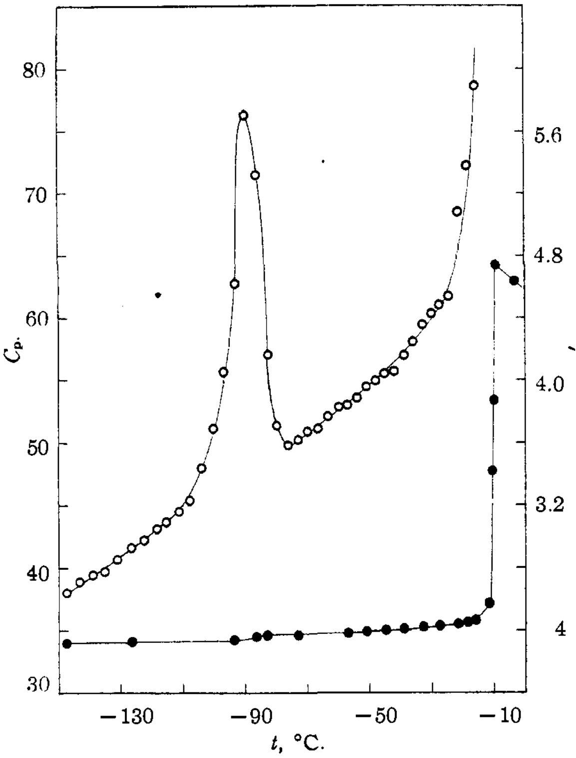

Fig. 5.—Temperature dependence of the dielectric constant and heat capacity of n-undecyl bromide. Hollow circles represent heat capacities and filled circles represent dielectric constants.

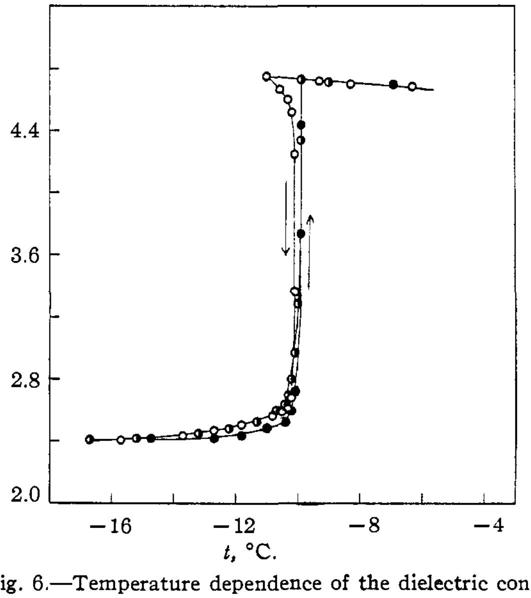

Fig. 6.—Temperature dependence of the dielectric constant of n-undecyl bromide near its melting point. Hollow circles are for cooling, half-filled circles for warming immediately after solidification, and filled circles for warming after eighteen hours at −196°.

higher value for the apparent heat of transition of n-undecyl bromide (Table IV) is probably due to the greater stability of the metastable form which prevents the gradual transformation of part of it into the stable form, thus increasing the quantity of material undergoing the transition in the metastable state. Some of the stable form was probably already present in the other compounds when the transitions took place, causing their apparent heats of transition to be lower than their true values, which would have been observed had only the metastable form been present. In a sense, the process occurring in these compounds may be compared with that occurring in organic glasses. The lower melting form is probably unstable throughout the entire temperature range in the solid, but the rate of growth of nuclei of the stable form is extremely slow at very low temperatures. On warming, however, a temperature is soon reached where the rate of growth becomes rapid and the change takes place spontaneously. Nuclei have evidently continued to form at low temperatures, and, therefore, their concentration is much higher on warming through the temperature region in which the change occurs than it was when the samples were cooled from the freezing points through the same region.

The heat capacity and dielectric constant results for n-octyl bromide, plotted in Fig. 7, show that this compound, although treated in the same manner as the odd members of the series,

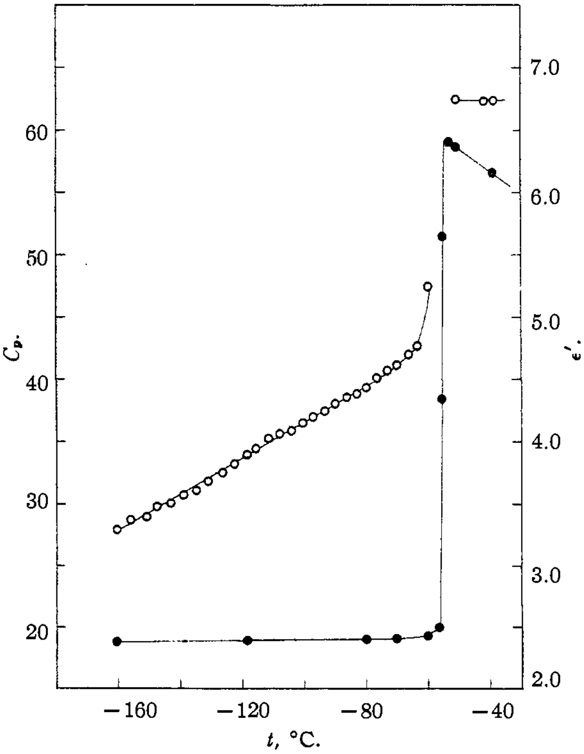

Fig. 7.—Temperature dependence of the dielectric constant and heat capacity of n-octyl bromide. Hollow circles represent heat capacities and filled circles represent dielectric constant.

does not exhibit polymorphism. The heat capacity rises normally in the solid through the entire temperature range. Dielectric constant data for *n*-octyl bromide and *n*-decyl bromide are shown in Figs. 8 and 9. In contrast to the odd members, somewhat more super-cooling was observed in these compounds. Although no heat capacity measurements were made on *n*-decyl bromide, it is believed that behavior similar to that found in *n*-octyl bromide exists. Deese[11] reports normal heat capacity behavior in *n*-butyl bromide and *n*-hexyl bromide. Dielectric constant measurements by Hoffman and Smyth[9] on *n*-dodecyl, *n*-hexadecyl and *n*-octadecyl bromides have shown that these substances also tend to super-cool a great deal before freezing and show no evidence of polymorphism. Any form such as that into which the odd members of the series freeze is evidently too unstable, and the temperature rises to the melting point of the stable form on solidification in the even members. The fact that the odd bromides show such a small amount of super-cooling probably means that the liquid structure possibly existing just above the solidification point is very similar to the structure of the crystals in the metastable forms.

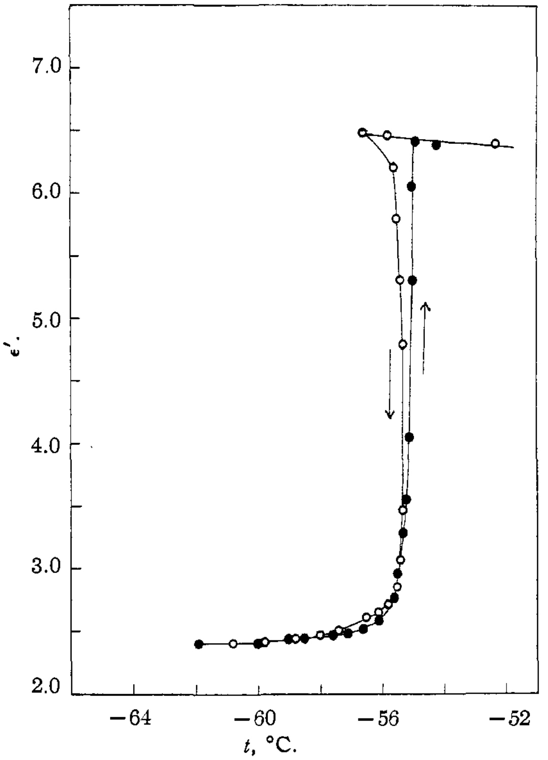

Fig. 8.—Temperature dependence of the dielectric constant of *n*-octyl bromide near its melting point. Hollow circles are for cooling and filled circles for warming.

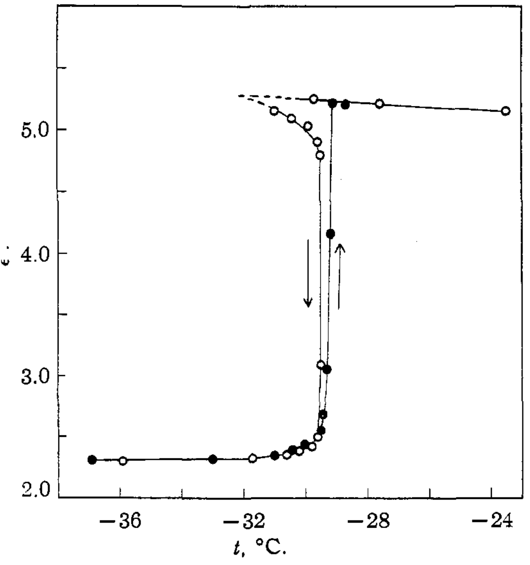

Fig. 9.—Temperature dependence of the dielectric constant of *n*-decyl bromide near its melting point. Hollow circles are for cooling and filled circles for warming.

The quantities of *n*-tridecyl bromide and *n*-pentadecyl bromide available for investigation were too small to permit heat capacity measurements. However, dielectric data were obtained for both compounds. These data are plotted in Figs. 10 and 11. A somewhat different phenomenon was observed in these members. Here again very little super-cooling was observed, the cooling curves being similar to those for *n*-heptyl, *n*-nonyl and *n*-undecyl bromides. On warming immediately, after cooling, the dielectric constant values in the solid agreed closely with the values obtained on cooling until the temperature reached about 0.2° below the freezing point. Instead of melting, however, each solid suddenly reverted to the stable form as indicated by a small drop or levelling off in dielectric constant and a shift over to the curve for the stable modification which melted at a slightly higher temperature. The difference between freezing and melting points, though small, is definitely greater than that occurring in *n*-octyl bromide and *n*-decyl bromide. After the samples had been allowed to stand for about twenty-four hours at liquid nitrogen temperatures, the dielectric constants on warming dropped to a significantly lower value in the solid. The compounds melted at the same temperature in both runs, however. It is evident that, in these higher members, the metastable form obtained on freezing is considerably less stable than in the lower members, making it impossible to melt this form. The melting points of the two forms in the lower odd members of the series converge quite rapidly from *n*-amyl bromide through *n*-nonyl bromide (Fig. 12). Since the higher melting form of *n*-undecyl bromide could not be isolated, it is possible that the phenomenon of the existence of a metastable form with an observable melting point terminates with this compound. If it continued to the higher members, one would expect the

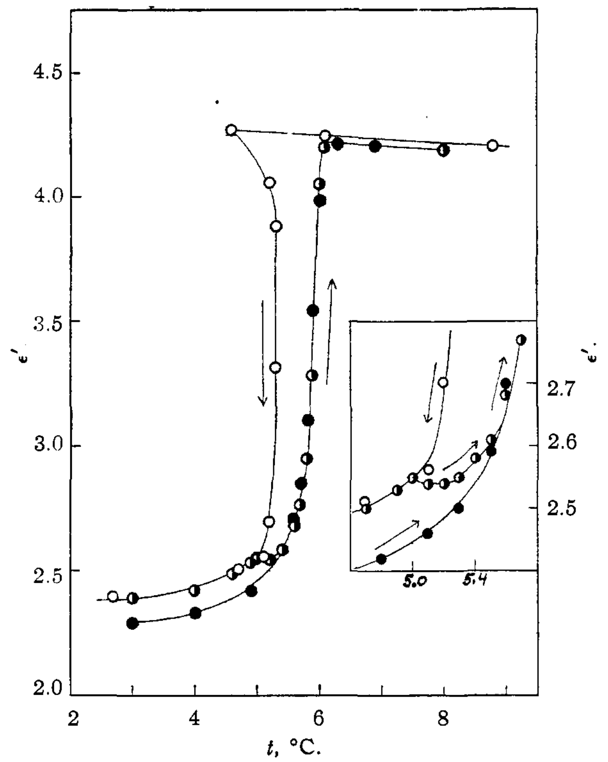

Fig. 10.—Temperature dependence of the dielectric constant of *n*-tridecyl bromide near its melting point. Hollow circles are for cooling, half-filled circles for warming immediately after solidification, and filled circles for warming after eighteen hours at −196°.

metastable forms of *n*-tridecyl and *n*-pentadecyl bromides to be extremely stable. This expectation is based on the increasing stability of the metastable forms with increasing chain length from *n*-heptyl through *n*-undecyl bromides.

An examination of Table I shows that the melting points usually reported for *n*-heptyl bromide and *n*-nonyl bromide are those of the metastable forms while for *n*-tridecyl bromide and *n*-pentadecyl bromide they are those of the stable form. This is to be expected, however, from simple warming and cooling curves since the metastable forms of the latter are only transient and evidence of their existence appears only on cooling. The melting point observed here for *n*-undecyl bromide, −9.9°, is considerably higher than that, −13.15°, previously reported.

Meyer and Reid[4] have observed a definite alternation of melting points for the bromide series, the odd members melting at nearly the same temperatures as the next higher even members. It was also observed that, beginning with *n*-tridecyl bromide, the melting points of the odd members were actually higher than the next higher even members. In this investigation, it was found that the stable form of *n*-nonyl bromide also melted slightly higher than *n*-decyl bromide. If it had been possible to isolate the higher melting form of *n*-undecyl bromide, its melting point probably would have been somewhat higher than that of *n*-dodecyl bromide, m. p. −9.6°. The alternation observed for these compounds is just the reverse of that found in the hydrocarbons. Malkin[21] has suggested that the essential difference between alternating and nonalternating series is that, in the former, the zigzag chain is tilted with respect to the terminal plane in the crystal. The existence of the various polymorphic forms is attributed, therefore, to differences in the angles of tilt of the hydrocarbon chains. Successive additions of methylene groups to these tilted chains result in an alternation in the long crystal spacings and consequently in the physical properties of such compounds in the solid state. Since polymorphism exists in the odd members of the bromide series, it seems probable that a difference in angle of tilt is involved.

The same type of reversed alternation in melting points has been observed for long-chain iodides. Malkin[22] has shown, by means of X-rays, that this reversal of the normal behavior is accompanied by a similar reversal in the long crystal spacings. A plot of these spacings against the

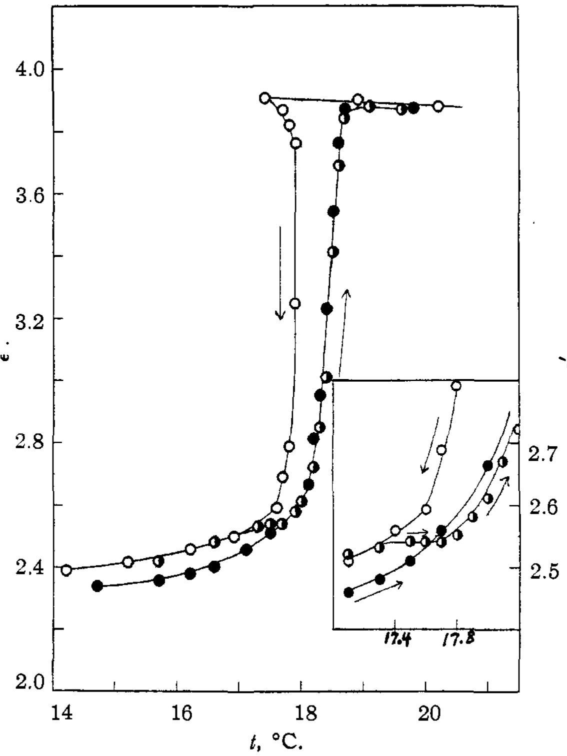

Fig. 11.—Temperature dependence of the dielectric constant of *n*-pentadecyl bromide near its melting point. Hollow circles are for cooling, half-filled circles for warming immediately after solidification, and filled circles for warming after eighteen hours at −196°.

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[21] Malkin, *Nature*, **127**, 126 (1939).

[22] Malkin, *J. Chem. Soc.*, 2796 (1931).

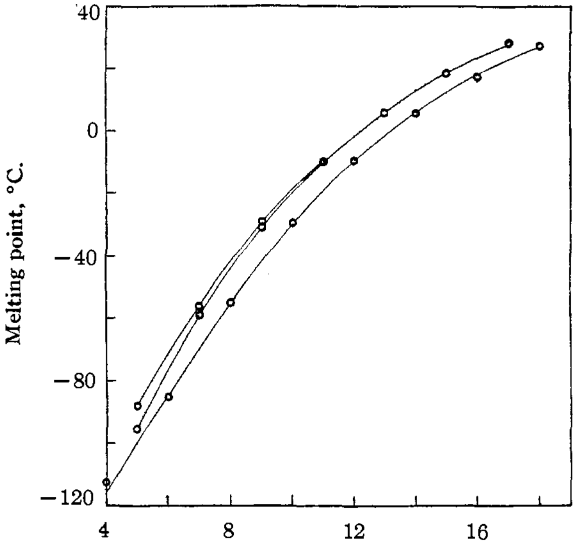

Fig. 12.—Melting points of *n*-alkyl bromides plotted against chain length.

number of carbon atoms shows that the line representing the even members is above that of the odd members. It was assumed that the iodine atom had the same effect as an additional methyl group, giving an even chain the properties of an odd. Since the size of the bromine atom is very nearly the same as that of the methyl group, the same argument can be used in explaining this same phenomenon in the bromides.

Phillips and Mumford[23] have observed two forms of *n*-hexadecyl chloride, the lower melting form appearing on cooling. An examination of this form showed it to be somewhat more transparent than the stable, higher melting form. Visual examination of the compounds investigated here showed that the metastable form possessed large, somewhat transparent crystals, which, on transforming to the stable form, became opaque masses of extremely small crystals, similar to those of the even members.

In a discussion of the results reported in this research, the effects of impurities cannot be disregarded. It has been frequently demonstrated that extremely small amounts of impurities will stabilize polymorphic forms in certain compounds. For example, small amounts of octadecane cause the formation of two crystalline forms in hexadecane.[24] The presence of a homolog stabilizes the metastable form of higher alcohols[24] and nitriles.[25] The profound influence of small traces of impurities on the polymorphic behavior of long-chain compounds raises the question as to whether the observations reported here may actually be a result of this. However, even if this is the case, it is still quite significant that polymorphism can be made to appear only in the odd members of the series. It was first thought that impurities might be stabilizing the metastable form in *n*-undecyl bromide. Examination of the dielectric constant–temperature curves in Fig. 6, however, leads one to believe that this cannot be the case. The melting and freezing points for this compound are extremely sharp. An alternative possibility is that impurities may actually decrease the stability of the lower melting form, as they have been observed to do in certain long chain secondary amines.[26] With this possibility in mind, a trace of *n*-dodecyl bromide was added to a purified sample of *n*-undecyl bromide. The only effect observed, however, was a slight depression of the freezing point as might be expected.

Summary

Simultaneous heat capacity and dielectric constant measurements have been made on *n*-heptyl, *n*-octyl, *n*-nonyl and *n*-undecyl bromides from liquid nitrogen temperature to temperatures well above their respective melting points. Heats of transition and fusion have been determined. The apparatus used for these measurements consisted of a combined heat conduction calorimeter and dielectric cell. Further dielectric constant measurements were made on these compounds and on *n*-decyl, *n*-tridecyl and *n*-pentadecyl bromides in the vicinity of their melting points with a low rate of change of temperature. These measurements have shown that the members of this series containing an odd number of carbon atoms exist in two polymorphic forms with different melting points. The metastable form in each case shows evidence of a small amount of orientational freedom below the melting points. The even members show no such properties. These findings may aid in clearing up some of the uncertainty existing in the literature melting points for these compounds.

PRINCETON, NEW JERSEY RECEIVED SEPTEMBER 12, 1949

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[23] Phillips and Mumford, *J. Chem. Soc.*, 1732 (1931).

[24] Smith, *ibid.*, 737 (1932).

[25] Hoffman, Hoerr and Ralston, THIS JOURNAL, **67**, 1542 (1945).

[26] Hoerr, Harwood and Ralston, *J. Org. Chem.*, **11**, 199 (1946).