921. *Physical Properties and Chemical Constitution. Part XXXI.* Polymethylene Dichlorides, Dibromides, Di-iodides, and Dicyanides.*

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Pure samples of a series of polymethylene dihalides (X·$[CH_2]_n$·X, where X = Cl, Br, or I) and dicyanides have been prepared; their refractive indices at 20° and their densities and surface tensions over a range of temperatures have been measured. The refractions, molecular refraction coefficients, and parachors for the carbon–halogen bond and carbon–nitrogen triple bond have been evaluated.

The present research was undertaken to secure trustworthy data on the physical properties of pure polymethylene halides and cyanides, to evaluate the bond refractions, bond molecular refraction coefficients, and bond parachors of C–Cl, C–Br, C–I, and C⋮N, and to

* Part XXX, preceding paper.

compare the values of the bond constants with those previously obtained from n-alkyl halides and cyanides.[1-3] The results for the bond constants, deduced with the aid of the CH_2 values given in Part XXIV,[1] are collected in Table 1; the corresponding figures for the monohalides and monocyanides are given in Table 2.

TABLE 1. *Bond parachors, bond refractions (at 20°), and bond refraction coefficients (at 20°) for* C–Cl, C–Br, C–I, *and* C⋮N *deduced from data on the dihalides and dicyanides.*

Bond	No. of compounds	P	$[R]_C$	$[R]_D$	$[R]_F$	$[R]_G$	Mn_D^{20}
C–Cl	7	55·6	6·44	6·46	6·57	6·61	57·52
C–Br	6	67·3	9·27	9·31	9·51	9·64	128·35
C–I	6	91·4	14·35	14·48	14·87	15·16	212·30
C⋮N	5	61·2	4·80	4·82	4·90	4·91	30·10

TABLE 2. *Bond constants for* C–Cl, C–Br, C–I, *and* C⋮N *deduced from data on the mono-halides and -cyanides.*

Bond	P	$[R]_C$	$[R]_D$	$[R]_F$	$[R]_{G'}$	Mn_D^{20}
C–Cl	57·4	6·48	6·51	6·58	6·64	56·80
C–Br	70·9	9·32	9·39	9·54	9·68	124·51
C–I	92·4	14·47	14·61	14·96	15·28	202·46
C⋮N	61·4	4·80	4·82	4·87	4·91	29·91

It will be noted that the bond constants for the carbon–halogen bonds in Table 2 are appreciably higher than those in Table 1; no explanation can be offered for these real differences.

The mean CH_2 values evaluated from the measurements in the four series of compounds, together with the standard deviation s, are collected in Table 3.

TABLE 3. *Mean values for* CH_2.

Compounds	P	$[R]_C$	$[R]_D$	$[R]_F$	$[R]_{G'}$	Mn_D^{20}
$Cl\cdot[CH_2]_n\cdot Cl$	41·5	4·62	4·64	4·69	4·73	20·69
s	0·3	0·01	0·01	0·02	0·02	0·16
$Br\cdot[CH_2]_n\cdot Br$	42·1	4·65	4·67	4·72	4·77	20·00
s	0·4	0·01	0·02	0·02	0·04	0·22
$I\cdot[CH_2]_n\cdot I$	41·6	4·63	4·65	4·70	4·74	17·87
s	0·2	0·01	0·01	0·01	0·01	1·03
$N{\vdots}C\cdot[CH_2]_n\cdot C{\vdots}N$	41·5	4·61	4·64	4·68	4·73	20·53
s	0·1	0·01	0·01	0·01	0·02	0·07

EXPERIMENTAL

Physical Measurements.—Full details are given in Part XXIV.[1] Unless otherwise stated, b. p.s are corrected. All the compounds were re-fractionated immediately before the measurements were made. Every compound was examined for impurities by vapour-phase chromatography (a Griffin & George VPC apparatus, Mark II, was employed) and by infrared spectroscopy, but none was found.

Polymethylene Glycols.—Ethylene glycol (B.D.H) (redistilled) had b. p. 197—199°; trimethylene glycol (Fluka), b. p. 213—215°; butane-1,4-diol (Kodak), b. p. 223—224·5°; pentane-1,5-diol (Kodak), b. p. 232—234°. The higher diols were prepared by reduction of the appropriate highly purified esters with lithium aluminium hydride in ether.

Ethyl pimelate was prepared from 1,5-dicyanopentane. Suberic acid, m. p. 141°, was obtained by hydrolysis of 1,6-dicyanohexane (obtained from 1,4-di-iodobutane and acetonitrile; see below). Azelaic acid (Kodak) was recrystallised and had m. p. 104°.

Polymethylene Dichlorides.—These were obtained in good yield by the action of redistilled thionyl chloride upon the pure glycol in the presence of a little pyridine.[4]

[1] Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514.
[2] Vogel, *J.*, 1948, 644.
[3] Jeffery and Vogel, *J.*, 1948, 674.
[4] Ahmad, Bumpus, and Strong, *J. Amer. Chem. Soc.*, 1948, **70**, 3391.

Polymethylene Dibromides.—The dibromides were prepared by adding the glycol to a mixture of constant-boiling hydrobromic acid and concentrated sulphuric acid at 0°; the mixture was kept for 24 hr. and then refluxed for 3 hr.[5] Kamm and Marvel's procedure [6] gave poor yields and much tar with butane-1,4-diol and higher glycols. 1,4-Dibromobutane, 1,5-dibromopentane, and 1,6-dibromohexane were also prepared by the phosphorus–bromine method;[7] the physical properties of the products were identical with those of materials obtained by use of hydrobromic acid–sulphuric acid.

Polymethylene Di-iodides.—Methylene iodide was prepared from iodoform,[8] and trimethylene di-iodide from trimethylene glycol and constant-boiling hydriodic acid.[2] The other di-iodides were obtained by the action of potassium iodide and orthophosphoric acid upon the glycols.[9]

Polymethylene Dicyanides.—The 1,3-, 1,4-, and 1,5-dicyano-compounds were prepared from the diols and aqueous-alcoholic potassium cyanide.[10] 1,6-Dicyanohexane and 1,7-dicyanoheptane were obtained from 1,4-dibromobutane and 1,5-dibromopentane, respectively, by interaction with acetonitrile and sodamide in liquid ammonia; [11] the small amount of cyclic nitrile was easily removed by fractional distillation.

Tables 4 and 5 summarise the physical properties of all the pure compounds investigated; the numbering of compounds in Clarendon type follows from Part XXIX.[12] Table 4 contains the b. p. (at 760 mm., unless otherwise stated), rounded values of the density and surface tension

TABLE 4.

Ref. no.	Compound (*n* in Table 3)	B. p./mm.	d_4^{20}	d_4^{40}	d_4^{60}	d_4^{85}	γ_{20}	γ_{40}	γ_{60}	γ_{85}	*P*	Notes
					Dichlorides							
770	3	120°	1·1845	1·1604	1·1362	1·1050	33·95	31·46	29·00	25·91	230·3	*a*
771	4	155°	1·1395	1·1177	1·0993	1·0722	35·41	33·08	30·72	27·78	272·0	*b*
772	5	73·5°/14	1·1004	1·0816	1·0601	1·0361	35·81	33·46	31·12	28·20	313·9	*c*
773	6	90°/14	1·0690	1·0509	1·0325	1·0102	35·98	33·70	31·32	28·44	355·5	*d*
774	7	99·5°/8	1·0452	1·0278	1·0109	0·9888	36·01	33·86	31·70	28·90	396·6	*e*
775	8	106·5°/6	1·0263	1·0104	0·9929	0·9717	36·12	34·00	31·88	29·27	437·7	
776	9	113°/3	1·0107	0·9945	0·9784	0·9576	36·51	34·46	32·41	29·83	480·3	*f*
					Dibromides							
777	2	131°	2·1789	2·1391	2·1000	2·0486	40·24	37·50	34·96	31·62	217·4 *	*g*
778	3	165°	1·9810	1·9474	1·9204	1·8693	39·95	37·52	35·14	32·12	256·6	*h*
779	4	80°	1·8266	1·9767	1·7718	1·7290	40·85	38·50	36·11	33·12	299·2	*i*
780	5	96·5°/10	1·7024	1·6757	1·6492	1·6161	40·56	38·30	36·02	33·20	341·5	*j*
781	6	114°/11	1·6026	1·5782	1·5531	1·5209	40·32	38·14	35·92	33·16	384·1	*k*
782	7	116·5°/6	1·5264	1·5032	1·4801	1·4500	40·28	38·11	35·96	33·26	426·3	*l*
783	8	131°/4	1·4630	1·4418	1·4190	1·3916	39·84	37·74	35·63	33·00	468·0	
784	9	127·5°/2	1·4114	1·3903	1·3692	1·3424	39·54	37·50	35·44	32·87	509·6	
					Di-iodides							
785	1	79·5°/17	3·3201	3·2693	3·2177	3·1523	67·00	63·75	60·50	56·52	231·6 *	*m*
786	3	71·5°/2	2·5742	2·5360	2·4981	2·4510	47·86	45·50	43·10	40·10	303·0	*n*
787	4	106·0°/6	2·3581	2·3241	2·2900	2·2476	47·07	44·80	42·51	39·62	344·9	*o*
788	5	127·5°/7	2·1820	2·1509	2·1212	2·0832	45·52	43·36	41·20	38·42	386·4	
789	6	133·5°/5	2·0425	2·0137	1·9855	1·9500	44·50	42·18	39·90	37·00	427·8	*p*
790	7	139·5°/3	1·9308	1·9038	1·8778	1·8436	43·92	41·75	39·57	36·80	469·7	
791	8	149·5°/3	1·8375	1·8130	1·7873	1·7530	43·25	41·17	39·10	36·48	511·4	
792	9	139·0°/1	1·7602	1·7360	1·7115	1·6809	42·51	40·52	38·57	36·05	553·1	
					Dicyanides							
793	3	106°/1	0·9871	0·9714	0·9573	0·9391	48·12	46·02	43·93	41·33	251·1	*q*
794	4	124°/1	0·9623	0·9478	0·9335	0·9157	45·92	44·00	42·04	39·60	292·7	
795	5	140°/2	0·9451	0·9316	0·9177	0·9022	44·75	42·70	40·68	38·10	334·4	*r*
796	6	128°/0·8	0·9316	0·9192	0·9053	0·8884	43·80	41·80	39·80	37·25	375·8	*s*
797	7	135°/0·7	0·9222	0·9087	0·8955	0·8787	42·82	40·78	38·75	36·15	417·1	*t*

[5] Nenitescu and Necsoin, *J. Amer. Chem. Soc.*, 1950, **72**, 3483.
[6] Kamm and Marvel, *Org. Synth.*, Coll. Vol. I, p. 28, John Wiley & Sons, New York, 1932.
[7] Vogel, " Practical Organic Chemistry," p. 281, Longmans, Green & Co., London, 3rd edn.
[8] Adams and Marvel, ref. 6, p. 350.
[9] Stone and Shechter, *Org. Synth.*, 1951, **31**, p. 31, John Wiley & Sons, New York, 1951.
[10] Kamm and Marvel, ref. 6, p. 521.
[11] Paul and Tchelitcheff, *Bull. Soc. chim. France*, 1949, 470.
[12] *J.*, 1960, 4719.

TABLE 5.

Ref. no.	n_C^{20}	n_D^{20}	n_F^{20}	$n_{G'}^{20}$	$[R]_C$	$[R]_D$	$[R]_F$	$[R]_G$	Mn_D^{20}	Notes
				Dichlorides						
770	1·44592	1·44873	1·45413	1·45882	25·46	25·57	25·84	26·07	163·70	*a*
771	1·45230	1·45466	1·46060	1·46539	30·09	30·22	30·56	30·84	184·47	*b*
772	1·45428	1·45666	1·46263	1·46736	34·73	34·88	35·28	35·59	205·12	*c*
773	1·45495	1·45733	1·46327	1·46799	39·35	39·53	39·98	40·33	225·62	*d*
774	1·45582	1·45828	1·46412	1·46887	43·96	44·17	44·65	45·04	246·59	*e*
775	1·45701	1·45938	1·46528	1·47000	48·59	48·81	49·34	49·77	267·24	
776	1·45776	1·46020	1·46606	1·47081	53·20	53·45	54·03	54·50	287·87	*f*
				Dibromides						
777	1·53475	1·53874	1·54879	1·55739	26·84 *	27·00 *	27·42 *	27·78 *	289·12 *	*g*
778	1·51965	1·52315	1·53179	1·54012	30·97	31·14	31·58	31·98	307·48	*h*
779	1·51551	1·51900	1·52746	1·53295	35·68	35·88	36·37	36·80	328·01	*i*
780	1·50933	1·51257	1·52074	1·52845	40·36	40·57	41·12	41·63	347·84	*j*
781	1·50327	1·50642	1·51432	1·52079	45·02	45·26	45·86	46·38	367·55	*k*
782	1·49950	1·50249	1·51028	1·51682	49·67	49·93	50·58	51·13	387·67	*l*
783	1·49618	1·49913	1·50674	1·51287	54·32	54·59	55·30	55·87	407·83	
784	1·49331	1·49630	1·50364	—	58·94	59·24	59·98	—	428·04	
				Di-iodides						
785	1·73098	1·74037	—	—	32·24 *	32·55 *	—	—	466·2 *	*m*
786	1·63567	1·64199	1·65859	1·67057	41·19 *	41·52 *	42·37 *	43·09 *	485·90 *	*n*
787	1·61551	1·62143	1·63661	1·64964	45·90	46·26	47·16	47·94	502·55	*o*
788	1·59629	1·60175	1·61568	1·62762	50·53	50·91	51·86	52·68	518·92	
789	1·58132	1·58640	1·59936	1·61040	55·17	55·56	56·56	57·40	536·20	*p*
790	1·56983	1·57455	1·58678	1·59728	59·80	60·21	61·26	62·14	554·28	
791	1·56028	1·56484	1·57651	1·58639	64·44	64·87	65·97	66·89	572·81	
792	1·55248	1·55687	1·56801	1·57754	69·04	69·50	70·64	71·61	591·73	
				Dicyanides						
793	1·43340	1·43562	1·44103	1·44540	24·80	24·91	25·18	25·40	135·11	*q*
794	1·43626	1·43854	1·44389	1·44828	29·40	29·53	29·85	30·10	155·57	
795	1·43921	1·44146	1·44685	1·45126	34·01	34·17	34·53	34·82	176·10	*r*
796	1·44142	1·44366	1·44914	1·45360	38·64	38·81	39·22	39·56	196·62	*s*
797	1·44379	1·44620	1·45156	1·45605	43·25	43·45	43·91	44·28	217·25	*t*

* Not used in the calculation of the mean values for C–X.

a Timmermans [13] gives d^{20} 1·1862, n_C 1·44692, γ^{20} 34·01; cf. ref. 2. *b* Tischtschenko and Tschurbakov [14] give d_4^{20} 1·1598, n_D^{20} 1·4566. *c* Hoss and Huffman [15] give d_4^{20} 1·1028, n_D^{20} 1·4563; cf. ref. 16. *d* Galanina [17] gives d_4^{20} 1·066, n_D^{20} 1·4620. *e* Galanina [17] gives d_4^{20} 1·048, n_D^{20} 1·4500. *f* Ahmad, Bumpus, and Strong [4] give n_D^{20} 1·4591. *g* Timmermans [13] gives d_4^{20} 2·1804, n_D^{20} 1·5387, γ^{20} 38·91; cf. ref. 2. *h* Smyth and Walls [18] give d_4^{25} 1·9701, n_D^{20} 1·52319; cf. ref. 2. *i* Smyth and Walls [18] give d_4^{25} 1·8177, n_D^{20} 1·51908; cf. ref. 2. *j* Smyth and Walls [18] give d_4^{25} 1·6927, n_D^{20} 1·51255; cf. refs. 19, 20. *k* Muller and Vanc [21] give d_4^{20} 1·6041, n_D^{20} 1·5069. *l* Muller and Vanc [21] give d_4^{20} 1·5306, n_D^{20} 1·5034. *m* Refractive indices n_F and $n_{G'}$ outside range of refractometer. Timmermans and Hennant-Roland [22] give n_D^{20} 1·74108; cf. ref. 2. *n* Cf. ref. 2. *o* Stone and Shechter [23] give d_4^{20} 2·300, n_D^{20} 1·615. *p* Stone and Shechter [23] give d_4^{20} 2·03, n_D^{20} 1·585; cf. ref. 24. *q* Cf. ref. 2. *r* Paul and Tchelitcheff [11] give d_4^{20} 0·948, n_D^{20} 1·4472. *s* Paul and Tchelitcheff [11] give d_4^{22} 0·940, n_D^{22} 1·4448. *t* Paul and Tchelitcheff [11] give d_4^{19} 0·929, n_D^{19} 1·4518.

at various temperatures, and the mean parachor; Table 5 gives the refractive indices, molar refractivities, and molar refraction coefficients.

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