285. *Physical Properties and Chemical Constitution. Part VI. Some Saturated and Unsaturated Cyano-esters.*

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The refractive indices for the C, D, F, and G′ lines at 20·0°, and the surface tensions and densities over a range of temperature, have been determined for the following compounds: ethyl cyanoacetate, ethyl α-cyano-ββ-dimethylpropionate, cyano-esters of the general formula $CR_1R_2{:}C(CN){\cdot}CO_2Et$ and $CHR_1R_2{\cdot}CH(CN){\cdot}CO_2Et$, where R_1R_2 = Me,Et, Et,Et, Me,Pr^a, Et,Pr^a, and Pr^a,Pr^a. The molecular refractivities and parachors have been evaluated.

The results now obtained are summarised in Table I; the calculated values of the parachor, P, based on Sugden's constants (J., 1924, **125**, 1180),* and of the molecular refractivities (Eisenlohr, *Z. physikal. Chem.*, 1910, **75**, 585; 1912, **79**, 129) are also included. It will be noted that (i) for most substances the observed parachor values are less than those calculated—the differences being far in excess of the experimental error of the

* Sugden's more recent values (see Mann and Purdie, J., 1935, 1549) are not sufficiently complete to permit the calculation of the parachors of the cyano-esters.

TABLE I.

	P.		$[R_L]_C$.		$[R_L]_D$.		$[R_L]_F$.		$[R_L]_{G'}$.		$Mn_D^{20°}$,
CR_1R_2:C(CN)·CO_2Et.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	obs.
R_1R_2 = Me,Et	403·0	407·8	45·73	44·41	46·03	44·65	46·80	45·19	47·44	45·65	245·40
= Et,Et	440·4	446·8	50·30	49·01	50·79	49·27	51·46	49·86	52·13	50·36	265·85
= Me,Pr^a	441·2	446·8	50·59	49·01	50·92	49·27	51·77	49·86	52·45	50·36	266·10
= Et,Pr^a	477·7	485·8	55·25	53·61	55·61	53·89	56·51	54·53	57·26	55·07	286·72
= Pr^a,Pr^a	516·6	524·8	59·99	58·21	60·19	58·50	61·34	59·20	62·15	59·78	307·16
CHR_1R_2·CH(CN)·CO_2Et.											
R_1R_2 = Me,Me	377·3	379·8	40·48	40·31	40·67	40·50	41·09	40·93	41·42	41·30	220·77
= Me,Et	414·3	418·8	44·90	44·91	45·10	45·12	45·58	45·60	45·92	46·01	241·65
= Et,Et	450·4	457·8	49·40	49·51	49·62	49·73	50·15	50·27	50·52	50·72	262·69
= Me,Pr^a	451·6	457·8	49·63	49·51	49·86	49·73	50·37	50·27	50·76	50·72	262·41
= Et,Pr^a	488·7	496·8	54·07	54·11	54·29	54·35	54·87	54·94	55·28	55·43	283·32
= Pr^a,Pr^a	527·1	535·8	58·98	58·71	59·42	58·97	59·90	59·60	60·39	60·14	304·25
CH_2(CN)·CO_2Et	262·4	262·8	26·63	26·52	26·74	26·64	27·03	26·93	27·24	27·17	160·35

determinations, and (ii) the molecular refractivities exhibit an exaltation for the unsaturated cyano-esters—this is probably due to the presence of the conjugated system >C=C—C≡N.

The various differences are shown in Table II. No comment is now made upon them except that attention is directed to the parachor differences, which are less than the accepted value of 39—40 units.

TABLE II.

CR_1R_2:C(CN)·CO_2Et.	Δ*P*.	$\Delta[R_L]_C$.	$\Delta[R_L]_D$.	$\Delta[R_L]_F$.	$\Delta[R_L]_{G'}$.	$\Delta Mn_D^{20°}$.
R_1R_2 = Me,Et } = Et,Et	37·4	4·57	4·76	4·66	4·69	20·45
= Et,Et } = Et,Pr^a	37·3	4·95	4·82	5·05	5·13	20·87
= Et,Pr^a } = Pr^a,Pr^a	38·9	4·74	4·58	4·83	4·89	20·44
R_1R_2 = Me,Et } = Me,Pr^a	38·2	4·86	4·89	4·97	5·01	20·70
= Me,Pr^a } = Et,Pr^a	36·5	4·66	4·69	4·74	4·81	20·62
CHR_1R_2·CH(CN)·CO_2Et.						
R_1R_2 = Me,Me } = Me,Et	37·0	4·42	4·43	4·49	4·50	20·88
= Me,Et } = Et,Et	36·1	4·50	4·52	4·57	4·60	21·04
= Et,Et } = Et,Pr^a	38·3	4·67	4·67	4·72	4·76	20·63
= Et,Pr^a } = Pr^a,Pr^a	38·4	4·91	5·13	5·03	5·11	20·93
R_1R_2 = Me,Me } = Me,Et	37·0	4·42	4·43	4·49	4·50	20·88
= Me,Et } = Me,Pr^a	37·3	4·73	4·76	4·79	4·84	20·76
= Me,Pr^a } = Et,Pr^a	37·1	4·44	4·43	4·50	4·52	20·91

EXPERIMENTAL.

Preparation of Unsaturated Cyano-esters, CR_1R_2:C(CN)·CO_2Et.—Most of these were prepared by the condensation of the appropriate ketone with ethyl cyanoacetate in the presence of anhydrous sodium sulphate and a little piperidine at 100°. Normal pressure was employed for acetone and methyl ethyl ketone; for the higher ketones the reaction was carried out in sealed pressure bottles. The unsaturated cyano-ester was separated by repeated fractionation through a Pyrex Scorah flask. Full experimental details will shortly be published.

Preparation of Saturated Cyano-esters, CHR_1R_2·CH(CN)·CO_2Et.—These were prepared by the reduction of the unsaturated cyano-esters with aluminium amalgam in moist ethereal solution (Vogel, J., 1927, 597) and purified by fractionation under diminished pressure.

Physical Measurements.—The densities, surface tensions, and refractive indices were determined as described in earlier papers of this series (compare Part III, J., 1938, 1325). The surface-tension apparatus *A*, *B*, and *C* were employed, the constants of which, when determined with pure benzene, were 1·8725, 2·3449, and 2·3740 respectively.

In the tabulated results, t is the temperature, h the observed difference in height (in mm.) in the two arms of the U-tube, H the corrected value, $d_{4^\circ}^{t^\circ}$ the density (calculated from the observed densities by assuming a linear variation with temperature), γ the surface tension (dynes/cm.) computed from the equation $\gamma = KHd$, P the parachor, M the molecular weight, and $Mn_D^{20\cdot0^\circ}$ the molecular refraction coefficient. The parachor was calculated in the usual way. The number in parentheses following the values of γ_{20° is the temperature coefficient of surface tension. All the measurements of the refractive indices were carried out at 20·0° ± 0·05°. Where 20° is used, 20·0° is to be understood; n_C, n_D, n_F, etc., are to be taken as referring to $n_C^{20\cdot0^\circ}$, etc., and R_C, etc., to $[R_L]_C$, etc.

Ethyl cyanoacetate. Boots's pure product was shaken several times with 10% sodium carbonate solution, washed well with water, dried (anhydrous sodium sulphate, shaking machine, 2 hours), and distilled from a fractionating Claisen flask. B. p. 85°/6 mm.; M = 113·12; n_C 1·41540, n_D 1·41751, n_F 1·42263, $n_{G'}$ 1·42639; R_C 26·63, R_D 26·74, R_F 27·03, $R_{G'}$ 27·24; $R_{G'-C}$ 0·61, R_{F-C} 0·40; $Mn_D^{20^\circ}$ 160·35.

Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0648, $d_{4^\circ}^{60\cdot1^\circ}$ 1·0262, $d_{4^\circ}^{87\cdot5^\circ}$ 0·9990, $d_{4^\circ}^{118\cdot5^\circ}$ 0·9682.

γ_{20° = 36·66 (0·11). Apparatus *B*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
19·1°	14·95	14·71	1·0657	36·76	261·4	88·5°	11·75	11·51	0·9980	29·21	263·5
61·9	13·53	13·29	1·0245	31·93	262·5						Mean 262·4

*Ethyl α-cyano-β-methyl-*n*-butyrate.* B. p. 78·5°/4 mm.; M = 155·19; n_C 1·42041, n_D 1·42256, n_F 1·42773, $n_{G'}$ 1·43160; R_C 40·48, R_D 40·67, R_F 41·09, $R_{G'}$ 41·42; $R_{G'-C}$ 0·94, R_{F-C} 0·61; $Mn_D^{20^\circ}$ 220·77.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9710, $d_{4^\circ}^{64\cdot1^\circ}$ 0·9307, $d_{4^\circ}^{86\cdot9^\circ}$ 0·9109.

γ_{20° = 30·46 (0·09$_1$). App. *C*.

19·8	13·46	13·22	0·9712	30·48	375·5	87·3	11·49	11·25	0·9105	24·32	378·5
61·6	12·28	12·04	0·9330	26·67	378·0						Mean 377·3

*Ethyl α-cyano-β-methyl-*n*-valerate.* B. p. 98°/6 mm.; M = 169·22; n_C 1·42576, n_D 1·42797, n_F 1·43316, $n_{G'}$ 1·43689; R_C 44·90, R_D 45·10, R_F 45·58, $R_{G'}$ 45·92; $R_{G'-C}$ 1·02, R_{F-C} 0·68; $Mn_D^{20^\circ}$ 241·65.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9653, $d_{4^\circ}^{61\cdot1^\circ}$ 0·9310, $d_{4^\circ}^{86\cdot9^\circ}$ 0·9089.

γ_{20° = 30·78 (0·08$_9$). App. *A*.

18·6	17·31	17·07	0·9666	30·90	412·7	86·9	14·75	14·51	0·9089	24·70	415·0
61·5	15·82	15·58	0·9306	27·15	415·3						Mean 414·3

*Ethyl α-cyano-β-ethyl-*n*-valerate.* B. p. 99°/4 mm.; M = 183·25; n_C 1·43127, n_D 1·43350, n_F 1·43880, $n_{G'}$ 1·44264, R_C 49·40, R_D 49·62, R_F 50·15, $R_{G'}$ 50·52; $R_{G'-C}$ 1·12, R_{F-C} 0·75; $Mn_D^{20^\circ}$ 262·69.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9608, $d_{4^\circ}^{61\cdot4^\circ}$ 0·9276, $d_{4^\circ}^{85\cdot7^\circ}$ 0·9084.

γ_{20° = 30·98 (0·09$_2$). App. *A*.

18·0	17·53	17·29	0·9624	31·16	449·9	85·7	14·90	14·66	0·9084	24·94	450·8
61·1	15·86	15·62	0·9279	27·14	450·8						Mean 450·4

*Ethyl α-cyano-β-methyl-*n*-hexoate.* B. p. 101·5°/4 mm.; M = 183·25; n_C 1·42976, n_D 1·43199, n_F 1·43722, $n_{G'}$ 1·44103; R_C 49·63, R_D 49·86, R_F 50·37, $R_{G'}$ 50·76; $R_{G'-C}$ 1·13, R_{F-C} 0·74; $Mn_{4^\circ}^{20^\circ}$ 262·41.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9534, $d_{4^\circ}^{61\cdot3^\circ}$ 0·9199, $d_{4^\circ}^{86\cdot5^\circ}$ 0·8991.

γ_{20° = 30·11 (0·08$_7$). App. *A*.

14·0	17·31	17·07	0·9583	30·63	449·9	87·0	14·66	14·42	0·8986	24·26	452·6
62·3	15·61	15·37	0·9190	26·45	452·2						Mean 451·6

Ethyl α-*cyano*-β-*ethyl*-n-*hexoate*. B. p. 108°/5·5 mm.; M = 197·27; n_C 1·43396, n_D 1·43620, n_F 1·44145, $n_{G'}$ 1·44531; R_C 54·07, R_D 54·29, R_F 54·87, $R_{G'}$ 55·28; $R_{G'-C}$ 1·21, R_{F-C} 0·80; $Mn_D^{20°}$ 283·32.

Densities determined : $d_{4°}^{20°}$ 0·9504, $d_{4°}^{62·1°}$ 0·9185, $d_{4°}^{87·3°}$ 0·8971.

$\gamma_{20°}$ = 30·49 (0·08$_8$). App. *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
15·0°	17·55	17·31	0·9543	30·93	487·5	86·1°	14·97	14·73	0·8978	24·76	490·2
61·2	15·81	15·57	0·9192	26·80	488·3					Mean	488·7

Ethyl α-*cyano*-β-n-*propyl*-n-*hexoate*. B. p. 120·5°/4 mm.; M = 211·30; n_C 1·43778, n_D 1·43993, n_F 1·44569, $n_{G'}$ 1·44994; R_C 58·98, R_D 59·42, R_F 59·90, $R_{G'}$ 60·39; $R_{G'-C}$ 1·41, R_{F-C} 0·92; $Mn_D^{20°}$ 304·25.

Densities determined : $d_{4°}^{20°}$ 0·9401, $d_{4°}^{61·6°}$ 0·9089, $d_{4°}^{86·5°}$ 0·8900.

$\gamma_{20°}$ = 30·06 (0·08$_6$). App. *A*.

20·4	17·30	17·06	0·9398	30·02	526·3	86·5	14·82	14·58	0·8900	24·30	527·1
62·0	15·86	15·62	0·9086	26·58	528·0					Mean	527·1

Ethyl α-*cyano*-β-*methyl*-β-*ethylacrylate*. B. p. 95·5°/3 mm.; M = 167·20; n_C 1·46410, n_D 1·46771, n_F 1·47685, $n_{G'}$ 1·48446; R_C 45·73, R_D 46·03, R_F 46·80, $R_{G'}$ 47·44; R_{G-C} 1·71, R_{F-C} 1·07; $Mn_D^{20°}$ 245·40.

Densities determined : $d_{4°}^{20°}$ 1·0091, $d_{4°}^{62·1°}$ 0·9699, $d_{4°}^{86·3°}$ 0·9488.

$\gamma_{20°}$ = 34·43 (0·10). App. *A*.

16·9	18·58	18·34	1·0119	34·75	401·2	85·5	15·91	15·67	0·9495	27·86	404·5
61·3	16·76	16·52	0·9706	30·02	403·2					Mean	403·0

Ethyl α-*cyano*-ββ-*diethylacrylate*. B. p. 96·5°/3 mm.; M = 181·23; n_C 1·46343, n_D 1·46692, n_F 1·47594, $n_{G'}$ 1·48327; R_C 50·30, R_D 50·79, R_F 51·46, $R_{G'}$ 52·13; $R_{G'-C}$ 1·83, R_{F-C} 1·16; $Mn_D^{20°}$ 265·85.

Densities determined : $d_{4°}^{20°}$ 0·9931, $d_{4°}^{63·1°}$ 0·9561, $d_{4°}^{86·9°}$ 0·9362.

$\gamma_{20°}$ = 33·53 (0·09$_8$). App. *A*.

19·1	18·30	18·06	0·9938	33·61	439·1	86·0	15·68	15·44	0·9370	27·09	441·3
62·0	16·64	16·40	0·9571	29·39	440·9					Mean	440·4

Ethyl α-*cyano*-β-*methyl*-β-n-*propylacrylate*. B. p. 100°/3 mm.; M = 181·23; n_C 1·46471, n_D 1·46829, n_F 1·47740, $n_{G'}$ 1·48484; R_C 50·59, R_D 50·92, R_F 51·77, $R_{G'}$ 52·45; $R_{G'-C}$ 1·86, R_{F-C} 1·18; $Mn_D^{20°}$ 266·10.

Densities determined : $d_{4°}^{20°}$ 0·9899, $d_{4°}^{63·1°}$ 0·9523, $d_{4°}^{85·5°}$ 0·9335.

$\gamma_{20°}$ = 33·21 (0·09$_3$). App. *A*.

19·3	18·18	17·94	0·9905	33·27	439·4	86·3	15·72	15·48	0·9328	27·04	443·
61·7	16·67	16·43	0·9536	29·34	441·2					Mean	441·2

Ethyl α-*cyano*-β-*ethyl*-β-n-*propylacrylate*. B. p. 104·5°/3 mm.; M = 195·26; n_C 1·46486, n_D 1·46839, n_F 1·47732, $n_{G'}$ 1·48468; R_C 55·25, R_D 55·61, R_F 56·51, $R_{G'}$ 57·26; $R_{G'-C}$ 2·01, R_{F-C} 1·26; $Mn_D^{20°}$ 286·72.

Densities determined : $d_{4°}^{20°}$ 0·9768, $d_{4°}^{62·4°}$ 0·9420, $d_{4°}^{86·3°}$ 0·9221.

$\gamma_{20°}$ = 32·46 (0·09$_9$). App. *A*.

19·7	18·00	17·76	0·9770	32·49	477·2	86·3	15·30	15·06	0·9221	26·00	478·2
61·9	16·25	16·01	0·9424	28·25	477·7					Mean	477·7

Ethyl α-*cyano*-ββ-*di*-n-*propylacrylate*. B. p. 116·5°/4 mm.; M = 209·28; n_C 1·46422, n_D 1·46771, n_F 1·47648, $n_{G'}$ 1·48380; R_C 59·99, R_D 60·19, R_F 61·34, $R_{G'}$ 62·15; $R_{G'-C}$ 2·16, R_{F-C} 1·35; $Mn_D^{20°}$ 307·16.

Densities determined : $d_{4°}^{20°}$ 0·9630, $d_{4°}^{63·1°}$ 0·9287, $d_{4°}^{85·3°}$ 0·9115.

$\gamma_{20°}$ = 31·81 (0·09$_5$). App. *A*.

18·7	17·83	17·69	0·9641	31·93	515·8	85·6	15·32	15·08	0·9113	25·73	517·2
61·7	16·19	15·95	0·9298	27·77	516·7					Mean	516·6

The authors' thanks are tendered to Imperial Chemical Industries Ltd. and to the Chemical Society for grants which have largely defrayed the cost of the research.

Woolwich Polytechnic, London, S.E. 18. [*Received, September 4th,* 1940.]