919. *Physical Properties and Chemical Constitution. Part XXIX.* Acetylenic Compounds.*

By Roman Grzeskowiak, George H. Jeffery, and Arthur I. Vogel.

Pure samples of a series of alk-1-ynes (hex-1-yne to tridec-1-yne), of prop-2-ynyl esters (formate to n-heptoate), and of but-2-yn-1,4-ylene diesters (diformate to di-n-heptoate) have been prepared, and their refractive indices at 20°, and densities and surface tensions over a range of temperatures, have been determined. The bond constants (refractions, molecular refraction coefficients, and parachors) for the carbon-to-carbon triple bond, both terminal and non-terminal, have been evaluated.

The present investigation was undertaken to secure trustworthy data on the physical properties of pure acetylenic compounds containing both terminal and non-terminal acetylenic groupings, and to evaluate the bond refractions, bond parachors, and bond molecular-refraction coefficients. Our initial measurements upon esters of but-3-yne-1-carboxylic acid and dec-9-yne-1-carboxylic acid [1] gave values for the various constants which were more trustworthy than those deduced by Campbell and Eveslage [2,3] from various acetylenic hydrocarbons. We now present the results deduced from measurements upon pure acetylenic hydrocarbons (hex-1-yne to tridec-1-yne) and upon prop-2-ynyl esters, which lead to values for the terminal carbon–carbon triple bond: in addition, values for non-terminal acetylenic groups have been evaluated from new measurements upon the but-2-yn-1,4-ylene diesters (formate to n-heptoate). All the results for the bond constants, including those given in Part XVII,[1] are collected in Table 1.

The mean CH_2 values deduced from the measurements in the three series of compounds, together with the standard deviation *s*, are collected in Table 2.

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* Part XXVIII, *J.*, 1960, 4454.

[1] Jeffery and Vogel, Part XVII, *J.*, 1948, 674.

[2] Campbell and Eveslage, *J. Amer. Chem. Soc.*, 1945, **67**, 1851.

[3] Cf. Hennion and Banigan, *J. Amer. Chem. Soc.*, 1946, **68**, 1381.

The bond constants for the carbon–carbon triple bond were calculated with the aid of the values given in Part XXIV.[4]

TABLE 1. *Bond parachors, bond refractions (at 20°), and bond refraction coefficients (at 20°) for the carbon–carbon triple bond.*

Series of compounds	No. of compounds	P	$[R]_C$	$[R]_D$	$[R]_F$	$[R]_{G'}$	Mn_D^{20}
$CH{\equiv}C{\cdot}[CH_2]_2{\cdot}CO_2R$ [1]	4	53·1	5·86	5·91	6·01	6·11	25·04
$CH{\equiv}C{\cdot}[CH_2]_8{\cdot}CO_2R$ [1]	3	54·0	5·75	5·80	5·91	6·00	25·06
$CH{\equiv}C{\cdot}[CH_2]_n{\cdot}CH_3$	8	51·0	5·79	5·82	6·00	6·04	24·75
Mean value of C⋮C (terminal)	15	$52{\cdot}1_6$	$5{\cdot}80_1$	$5{\cdot}84_0$	$5{\cdot}91_8$	$6{\cdot}05_0$	$24{\cdot}88_8$
$CH_3{\cdot}C{\equiv}C{\cdot}O{\cdot}COR$	5	55·4	5·83	5·85	6·02	6·07	25·43
$R{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}O{\cdot}COR$ ...	5	51·1	6·40	6·40	6·59	6·68	27·45

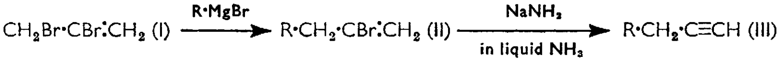
TABLE 2. *Mean values for* CH_2.

Compounds	No. of compounds	P	$[R]_C$	$[R]_D$	$[R]_F$	$[R]_{G'}$	Mn_D^{20}
$CH{\equiv}C{\cdot}[CH_2]_n{\cdot}CH_3$	8	40·1	4·62	4·64	4·69	4·73	20·61
s		0·5	0·01	0·01	0·01	0·02	0·05
$CH_3{\cdot}C{\equiv}C{\cdot}O{\cdot}COR$	5	38·8	4·62	4·65	4·70	4·74	20·50
s		0·2	0·01	0·01	0·02	0·02	0·13
$R{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}O{\cdot}COR$ ...	5	38·4	4·63	4·65	4·70	4·74	20·47
s		1·1	0·01	0·01	0·01	$0{\cdot}00_4$	0·2

EXPERIMENTAL

Physical Measurements.—Full details are given in Part XXVIII.[5] Unless otherwise stated, b. p.s are corrected. All the compounds were refractionated immediately before the measurements were made. The purity of every compound was established by vapour-phase chromatography (a Griffin & George VPC apparatus, Mark II, was employed) and by infrared spectroscopy.

*Preparation of Alk-*1*-ynes (Hept-*1*-yne to Tridec-*1*-yne, and* 3*-Cyclohexylprop-*1*-yne).*—All the alkynes were prepared in accordance with the following scheme:



$$CH_2Br{\cdot}CBr{:}CH_2\ (I) \xrightarrow{R{\cdot}MgBr} R{\cdot}CH_2{\cdot}CBr{:}CH_2\ (II) \xrightarrow[\text{in liquid } NH_3]{NaNH_2} R{\cdot}CH_2{\cdot}C{\equiv}CH\ (III)$$

2,3-Dibromopropene[6] when treated with the appropriate Grignard reagent gave the 2-bromoalk-1-ene (II),[7] and the latter afforded the alk-1-yne with sodamide in liquid ammonia solution.[8,9] The use of sodamide in liquid ammonia for dehydrohalogenation gives a better yield and is much more convenient than that involving a suspension of finely pulverised sodamide in a purified mineral oil of b. p. >250°.[8,10] The alcohols employed in the preparation of the Grignard reagents were highly purified commercial products.

*Preparation of Hex-*1*-yne.*—The above general procedure gave a very poor yield of hex-1-yne. It was prepared from n-butyl bromide and sodium acetylide[11] on a large scale, and the pure hydrocarbon was isolated by fractionation through a long Fenske column.

*Esters of Prop-*2*-yn-*1*-ol with Aliphatic Monocarboxylic Acids.*—The esters (except formate) were prepared in good yield by azeotropic distillation of the alcohol (b. p. 114°/760 mm.) and the pure acid in benzene in the presence of ZeoKarb 225(H) as catalyst.[12] For the acetate and propionate, 2 mol. of acid to 1 mol. of alcohol were used: for esters of the higher acids, excess of alcohol (which is readily separated from the ester by fractional distillation) was employed.

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[4] Vogel, Cresswell, Jeffery, and Leicester, Part XXIV, *J.*, 1952, 14.

[5] Kyte, Jeffery, and Vogel, *J.*, 1960, 4454.

[6] *Org. Synth.*, Coll. Vol., 1941, 2nd edn., 209.

[7] Cf. *ibid.*, p. 186.

[8] Cf. *ibid.*, p. 191.

[9] Vaughn, Vogt, and Newland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120.

[10] Bourguel, *Ann. Chim. (France)*, 1925, **3**, 231.

[11] Vogel, " Practical Organic Chemistry," 3rd edn., 1957, Longmans, Green & Co., p. 897.

[12] Sussmann, *Ind. Eng. Chem.*, 1946, **38**, 1229.

TABLE 3.

Ref. no.	Compound	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
	Hydrocarbons											
746	Hex-1-yne	71·5°	0·7150	—	—	—	20·98	—	—	—	245·8	*a*
747	Hept-1-yne	99·5°	0·7329	0·7149	0·6969	—	22·67	20·61	18·50	—	286·2	*b*
748	Oct-1-yne	124·5°	0·7462	0·7298	0·7125	0·6914	23·86	21·78	19·70	—	326·3	*c*
749	Non-1-yne	57°/25	0·7580	0·7423	0·7261	0·7047	25·00	23·02	21·05	18·60	366·5	*d*
750	Dec-1-yne	73·5°/25	0·7661	0·7510	0·7353	0·7154	25·95	24·00	22·07	19·67	407·2	*e*
751	Undec-1-yne	94·5°/25	0·7729	0·7580	0·7425	0·7235	26·58	24·71	22·82	20·48	447·2	
752	Dodec-1-yne	113·5°/25	0·7787	0·7650	0·7503	0·7317	27·18	25·33	23·49	21·12	487·3	*g*
753	Tridec-1-yne	125°/25	0·7844	0·7707	0·7562	0·7380	27·55	25·69	23·81	21·46	526·8	*h*
754	3-Cyclohexyl-prop-1-yne	55°/21	0·8445	0·8285	0·8120	0·7925	29·80	27·84	25·90	23·48	338·6 *	
	Esters of prop-2-yn-1-ol											
755	Formate	105·5°	1·0452	1·0218	0·9986	0·9700	35·00	32·17	29·34	—	195·8 *	
756	Acetate	121·5°	0·9982	0·9761	0·9541	0·9275	32·81	30·20	27·58	—	235·2 *	
757	Propionate	138·5°	0·9726	0·9515	0·9297	0·9022	31·27	28·82	26·44	23·44	272·8	
758	Butyrate	156·0°	0·9495	0·9299	0·9098	0·8837	30·04	27·83	25·66	22·90	311·4	
759	Valerate	84·0°/25	0·9360	0·9176	0·8985	0·8752	29·78	27·69	25·61	22·98	350·2	
760	Hexanoate	97·5°/25	0·9248	0·9075	0·8892	0·8668	29·52	27·51	25·52	23·01	389·2	
761	Heptanoate	112·0°/25	0·9172	0·9015	0·8831	0·8620	29·66	27·78	25·90	23·52	428·0	
762	Prop-2-yn-1-ol	113·5°	0·9475	0·9308	0·9115	0·8905	36·04	33·50	30·98	—	144·9 *	
	Diesters of but-2-yne-1,4-diol											
763	Formate	86°/1	1·2244	1·2036	1·1825	1·1562	—	45·65	42·74	39·15	306·3 *	*j*
764	Acetate	116°/4	1·1263	1·1070	1·0869	1·0631	—	38·20	35·78	32·71	381·8 *	*k*
765	Propionate	120°/2	1·0701	1·0513	1·0331	1·0062	36·16	34·07	31·98	29·38	453·6	
766	Butyrate	116°/1	1·0277	1·0094	0·9918	0·9698	33·14	31·42	29·70	27·50	528·0	
767	Valerate	134°/1	1·0024	0·9863	0·9695	0·9478	32·02	30·40	28·88	26·71	604·0	
768	Hexanoate	158°/1	0·9814	0·9656	0·9503	0·9303	31·48	29·87	28·22	26·15	681·0	
769	Heptanoate	175°/1	0·9655	0·9508	0·9355	0·9165	31·23	29·80	28·35	26·51	760·5	

* Not used in the calculation of the mean values for (CH_2) and for ($C\equiv C$).

a d_4^{14} 0·7203; γ_{14} 21·80; Campbell and Eby (*J. Amer. Chem. Soc.*, 1941, **63**, 2684) give d_4^{20} 0·71518, n_D^{20} 1·39840; cf. Henne and Greenlee (*ibid.*, 1945, **67**, 485), Levina *et al.* [*J. Gen. Chem.* (*U.S.S.R.*), 1951, **21**, 240]. *b* Campbell and Eby (*loc. cit.*) give d_4^{20} 0·73379, n_D^{20} 1·40840; cf. refs. 14, 15. *c* Campbell and Eby (*loc. cit.*) give d_4^{20} 0·7463, n_D^{20} 1·41565; cf. refs. 14, 16. *d* Elsner and Paul (*J.*, 1951, 893) give n_D^{20} 1·4224; cf. ref. 10. *e* Elsner and Paul (*loc. cit.*) give n_D^{20} 1·4269; cf. ref. 17. *f* Brown, Greenlee, and Fusari (*J. Amer. Oil Chemists' Soc.*, 1951, **28**, 416) give n_D^{20} 1·4328. *g* Brown, Greenlee, and Fusari (*loc. cit.*) give n_D^{20} 1·4343; cf. ref. 17. *h* Elsner and Paul (*loc. cit.*) give n_D^{20} 1·4374; cf. Lamb and Smith (*J.*, 1952, 5032). *i* Henne and Greenlee (*loc. cit.*) give d_4^{20} 0·9478, n_D^{20} 1·4320; cf. Hennion and Murray (*J. Amer. Chem. Soc.*, 1942, **64**, 1220). *j* M. p. 35·5°. Refractive index values at 20° are for the supercooled liquid; n_D^{35} 1·45441; d_4^{20} obtained by extrapolation. *k* M. p. 28·3°. Refractive index values at 20° are for the supercooled liquid; n_D^{35} 1·44822; d_4^{20} obtained by extrapolation. Hennion and Kupiecki (*J. Org. Chem.*, 1953, **18**, 1601) give n_D^{25} 1·4512; d^{25} 1·1223; cf. Johnson, *J.*, 1946, 1009.

In all cases, the cation-exchange resin was filtered off after water ceased to distil into the Dean and Stark tube: for the acetate and propionate, the excess of acid was removed by shaking the mixture with excess of sodium hydrogen carbonate solution, and the neutral product washed with water, dried, and fractionated. For the n-butyrate and higher esters, the crude ester fraction was first isolated by fractionation, washed with water, dried, and fractionated again. Since formic acid is not miscible with benzene, the ester was prepared by refluxing the alcohol with excess of acid in methylene chloride solution for 14 hr., and the ester isolated in the usual manner (yield 50%).

The following esters are new: *formate* (Found: C, 57·4; H, 4·8. $C_4H_4O_2$ requires C, 57·2; H, 4·8%); *propionate* (Found: C, 64·4; H, 7·3. $C_6H_8O_2$ requires C, 64·4; H, 7·2%); *butyrate* (Found: C, 66·5; H, 8·0. $C_7H_{10}O_2$ requires C, 66·6; H, 7·9%); *valerate* (Found: C, 68·8; H, 8·6. $C_8H_{12}O_2$ requires C, 68·6; H, 8·6%); *hexanoate* (Found: C, 70·2; H, 9·1. $C_9H_{14}O_2$ requires C, 70·0; H, 9·1%); and *heptanoate* (Found: C, 71·1; H, 9·7. $C_{10}H_{16}O_2$ requires C, 71·3; H, 9·6%).

Diesters of But-2-yne-1,4-diol with Aliphatic Monocarboxylic Acids.—The procedure adopted was similar to that described for prop-2-ynyl esters: benzene was used as solvent for all esters except the diformate, for which methylene chloride was satisfactory. The proportions used were butynediol, m. p. 54°, 1 mol., and acid 5—6 mol. After 25—30 hours' refluxing, the cation-exchange resin was filtered off: for the diformate and the diacetate, the reaction product was neutralised with saturated sodium hydrogen carbonate solution, washed with water, dried, and fractionated. For the higher esters, the solvent was removed by distillation at atmospheric pressure, and the excess of acid at 2 mm.: the residual ester was washed with saturated sodium hydrogen carbonate solution until neutral, then with water, dried, and fractionally distilled. The yields in all cases were excellent.

TABLE 4.

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
					Hydrocarbons					
746	1·39649	1·39881	1·40451	1·40915	27·63	27·78	28·13	28·41	114·90	*a*
747	1·40641	1·40874	1·41448	1·41912	32·25	32·42	32·82	33·14	135·47	*b*
748	1·41355	1·41591	1·42163	1·42627	36·87	37·05	37·49	37·86	156·02	*c*
749	1·42010	1·42246	1·42819	1·43281	41·48	41·69	42·18	42·58	176·70	*d*
750	1·42467	1·42703	1·43279	1·43748	46·11	46·34	46·88	47·32	197·27	*e*
751	1·42853	1·43089	1·43665	1·44134	50·74	50·99	51·58	52·06	217·88	*f*
752	1·43199	1·43436	1·44013	1·44485	55·38	55·65	56·29	56·82	238·53	*g*
753	1·43505	1·43742	1·44322	1·44789	55·99	60·28	60·97	61·52	259·20	*h*
754	1·45644	1·45894	1·46535	1·47035	39·37 *	39·55 *	40·03 *	40·40 *	178·30 *	
					Esters of prop-2-yn-1-ol					
755	1·41419	1·41670	1·42293	1·42780	20·11 *	20·21 *	20·48 *	20·69 *	119·10 *	
756	1·41624	1·41866	1·42468	1·42945	24·67 *	24·80 *	25·11 *	25·36 *	139·17	
757	1·42089	1·42331	1·42922	1·43392	29·23	29·37	29·73	30·02	159·58	
758	1·42343	1·42580	1·43173	1·43645	33·87	34·03	34·45	34·78	179·90	
759	1·42769	1·43013	1·43601	1·44077	38·50	38·69	39·15	39·53	200·47	
760	1·43058	1·43304	1·43886	1·44358	43·12	43·34	43·84	44·25	220·97	
761	1·43365	1·43611	1·44191	1·44652	47·73	47·97	48·52	48·96	241·60	
762	1·42950	1·43211	1·43880	1·44389	15·27 *	15·35 *	15·63 *	15·71 *	80·29 *	*i*
					Diesters of but-2-yne-1,4-diol					
763	1·45729	1·46001	1·46890	1·47213	31·63 *	31·79 *	32·20 *	32·51 *	207·40 *	*j*
764	1·45135	1·45390	1·46042	1·46544	40·71 *	40·91 *	41·41 *	41·80 *	247·40	*k*
765	1·45097	1·45343	1·45975	1·46468	49·87	50·11	50·71	51·18	288·09	
766	1·44962	1·45208	1·45828	1·46323	59·12	59·40	60·11	60·66	328·55	
767	1·45140	1·45385	1·46009	1·46490	68·36	68·69	69·50	70·14	369·75	
768	1·45218	1·45464	1·46072	1·46559	77·65	78·00	78·91	79·63	410·72	
769	1·45309	1·45558	1·46160	1·46641	86·91	87·32	88·32	89·11	451·84	

a—*k* See Table 3.

The following esters are new: *diformate* (Found: C, 50·7; H, 4·4. $C_6H_6O_4$ requires C, 50·6; H, 4·2%); *dipropionate* (Found: C, 60·6; H, 6·9. $C_{10}H_{14}O_4$ requires C, 60·5; H, 7·0%); *dibutyrate* (Found: C, 63·5; H, 8·2. $C_{12}H_{18}O_4$ requires C, 63·5; H, 8·0%); *divalerate* (Found: C, 66·0; H, 8·5. $C_{14}H_{20}O_4$ requires C, 66·0; H, 8·6%); *dihexanoate* (Found: C, 67·6; H, 9·2. $C_{16}H_{26}O_4$ requires C, 67·9; H, 9·2%); and *diheptanoate* (Found: C, 69·6; H, 9·6. $C_{18}H_{30}O_4$ requires C, 69·6; H, 9·6%).

Tables **3** and **4** summarise the physical properties of all the pure acetylenic compounds investigated; the numbering of compounds in Clarendon type follows from Part XXVIII.[5] Table **3** contains the b. p. (at 760 mm., unless otherwise stated), rounded values of the density, and surface tension at various temperatures, and the mean parachor; and Table **4** gives the refractive indices, molar refractivities, and the molar refraction coefficients.

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