127. *Physical Properties and Chemical Constitution. Part X.* n-*Alkylbenzenes.*

By Arthur I. Vogel.

n-Alkylbenzenes (toluene to *n*-hexylbenzene) have been prepared in a high degree of purity and their parachors and refractivities measured. The data give for CH_2 : *P* 39·2, R_C 4·625, R_D 4·645, R_F 4·699, $R_{G'}$ 4·734, and $Mn_D^{20^\circ}$ 20·66.

The normal alkylbenzenes have been prepared, with one exception, by Clemmensen reduction of the appropriate purified keto-compounds as follows: toluene from benzaldehyde; ethylbenzene from acetophenone; *n*-propylbenzene from propiophenone and from benzyl methyl ketone * and also from benzylmagnesium chloride and ethyl sulphate; *n*-butylbenzene from butyrophenone and from benzyl ethyl ketone *; *n*-amylbenzene from valerophenone and from benzyl *n*-propyl ketone *; *n*-hexylbenzene from 2-phenylethyl *n*-propyl ketone. Where more than one method of preparation has been employed, the procedure considered to give the purest product has been indicated by an asterisk. The parachors and refractivities have been determined. The results are summarised in the following table; molecular refractivities refer to a temperature of 20°. The mean values of the CH_2 increment have been calculated by the method of least squares. The final values given in Part IX (*J.*, 1946, 133) from the data on *n*-aliphatic hydrocarbons and *n*-alkyl halides were *P* 40·0, R_C 4·624, R_D 4·647, R_F 4·695, $R_{G'}$ 4·735, and $Mn_D^{20^\circ}$ 20·59.

Parachors and refractivities of normal alkylbenzenes.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20^\circ}$.
$C_6H_5{\cdot}CH_3$	245·4	30·86	31·10	31·70	32·19	137·89
$C_6H_5{\cdot}CH_2{\cdot}CH_3$	284·3	35·49	35·75	36·41	37·03	158·82
$C_6H_5{\cdot}[CH_2]_2{\cdot}CH_3$	323·2	40·15	40·43	41·16	41·73	179·29
$C_6H_5{\cdot}[CH_2]_3{\cdot}CH_3$	362·0	44·78	45·08	45·85	46·47	199·92
$C_6H_5{\cdot}[CH_2]_4{\cdot}CH_3$	402·0	49·40	49·73	50·56	51·21	220·64
$C_6H_5{\cdot}[CH_2]_5{\cdot}CH_3$	441·5	53·95	54·29	55·15	55·86	241·35

Mean values for CH_2 *calculated by the method of least squares.*

CH_2	39·2	4·625	4·645	4·699	4·734	20·66

The present communication forms one of a series, the objects of which include: (1) The provision of trustworthy data (parachors and refractivities) for various classes of compounds specifically selected in the first instance for the calculation of atomic, group, and structural constants. (2) The evaluation of atomic, group, and structural constants with particular reference to the parachor and to the refractivities for the C, D, F, and G′ lines. (3) The evaluation of the refractions of electron bonds and electron groups according to von Steiger (*Ber.*, 1921, **54**, 1381), Smyth (*Phil. Mag.*, 1925, **50**, 715; " Dielectric Constant and Molecular Structure," 1931, 150), and Fajans and Knorr (*Ber.*, 1926, **59**, 249), and of bond refractions after the procedure of Denbigh (*Trans. Faraday Soc.*, 1940, **36**, 397). (4) The application of such constants, based exclusively upon the author's own measurements, to structural and constitutional problems.

The mean values of the refractivities for CH_2 given in Part IX (*loc. cit.*) lead to the following refractions for the C–H bond (in CH_2) and the C–C bond at 20° :

	R_C.	R_D.	R_F.	$R_{G'}$.
C–H (in CH_2)	1·669	1·676	1·693	1·704
C–C	1·286	1·296	1·301	1·328

These figures will form the basis of all calculations of bond refractions. For C–H and C–C respectively Smyth (*loc. cit.*) gives 1·705 and 1·209, whilst Fajans and Knorr (*loc. cit.*) deduce 1·704 and 1·209 : these values presumably refer to the D sodium line. Since these fundamental constants are clearly in error, all their calculations of the refractions of electron groups must be regarded as very approximate. Denbigh (*loc. cit.*) calculates 1·69 for C–H and 1·25 for C–C directly from the molecular refractions.

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* The numbering of compounds in Clarendon type follows from Part IX (*J.*, 1946, 135). Reference to compounds, the preparation of which is described in preceding or succeeding papers of this series, will be abbreviated to, *e.g.*, IX, **101**.

EXPERIMENTAL.

Physical Measurements.—Full details applying to this and the subsequent papers of this series are given in Part VII (*J.*, 1943, 18). Surface tensions were measured by the method of capillary rise, and only the values for H ($= h - 0{\cdot}24$ mm.) are given. The constants for the various apparatus are: *A* 1·8725, *B* 2·3449, *C*, 2·3740, *D* 2·4696, *E* 2·3290. Unless otherwise stated, all b. p.s are corrected. All measurements of the refractive indices were made at 20° ± 0·02° on a Zeiss Pulfrich refractometer. It should be pointed out that measurements upon aromatic compounds, *e.g.*, phenyl alkyl ketones (following paper), phenyl alkyl ethers (Part XII, this vol., p. 616), and even upon alkylbenzenes, especially for the lower homologues, are frequently difficult because of the small separation of the lines with the prism IIf employed: the G′ line is often very faint and adjustment to the crosswires is not a precise operation. The values for $n_{G'}$, in some cases, may, in consequence, be subject to appreciable error. This difficulty of measurement is absent in the new Hilger–Chance refractometer, and it is hoped to repeat the measurements when the instrument is available commercially.

In the tabulated results, t is the temperature, h is the observed difference in height (in mm.) in the two arms of the U-tube, H ($= h - 0{\cdot}24$) is 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 $Mn_{D}^{20^\circ}$ the molecular refraction coefficient. The parachor was calculated in the usual way, allowance for the density of the vapour (computed by Sugden's method, *J.*, 1925, **127**, 1540) being made when the temperature of the measurement was within 60° of the b. p. Where 20° is used, 20·0° is to be understood; n_C, n_D, n_F, $n_{G'}$ are to be taken as referring to $n_C^{20{\cdot}0^\circ}$, etc.; and R_C, etc. to $[R_L]_C$. Unless otherwise stated, all b. p.s are corrected.

Previous Work.—The larger proportion of the measurements described in this and succeeding papers of this series are new. The constants deduced will in all cases be based upon the author's own measurements. In order to economise space no reference will be made (save in exceptional circumstances) to previous work, since these can be readily found in I.C.T., Landolt–Börnstein " Tabellen ", or the original literature.

117.* *Toluene.*—100 G. of purified and redistilled benzaldehyde, b. p. 179°/757 mm., were reduced with 200 g. of amalgamated zinc and concentrated hydrochloric acid (IX, **101**); the yield of crude toluene was 43 g. of b. p. 109—110°/748 mm. This was washed with 10% of its volume of concentrated sulphuric acid until the washings were colourless (two washings required), then successively with water, 10% sodium carbonate solution, and water, and finally dried ($MgSO_4$). It was then *twice* distilled from sodium and passed over constantly in the second distillation at 110°/763 mm.; a middle fraction was used for the physical measurements.

B. p. 110°/763 mm.; M 92·13; n_C 1·49216, n_D 1·49669, n_F 1·50817, $n_{G'}$ 1·51743; R_C 30·86, R_D 31·10, R_F 31·70, $R_{G'}$ 32·19; $Mn_D^{20^\circ}$ 137·89. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8665, $d_{4^\circ}^{41{\cdot}0^\circ}$ 0·8483, $d_{4^\circ}^{60{\cdot}0^\circ}$ 0·8310, $d_{4^\circ}^{86{\cdot}0^\circ}$ 0·8071. Apparatus *A*.

(These headings apply to the corresponding columns in all the following tables.)

t.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.	t.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.
18·7°	17·68	0·8675	28·72	245·9	60·8°	15·27	0·8303	23·74	245·0
24·9	17·35	0·8621	28·01	245·8	86·4	13·84	0·8067	20·91	244·8
41·2	16·38	0·8481	26·01	245·3				Mean	245·4

118. *Ethylbenzene.*—100 G. of acetophenone, b. p. 200°/760 mm., when reduced as above, yielded 53 g. of crude ethylbenzene, b. p. 134·5—135°/758 mm. This was shaken with 6-ml. portions of concentrated sulphuric acid until the acid layer was colourless, and the pure hydrocarbon was isolated as detailed under toluene.

B. p. 135°/755 mm.; M 106·16; n_C 1·49170, n_D 1·49598, n_F 1·50686, $n_{G'}$ 1·51567; R_C 35·49, R_D 35·75, R_F 36·41, $R_{G'}$ 37·03; $Mn_D^{20^\circ}$ 158·82. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8675, $d_{4^\circ}^{41{\cdot}0^\circ}$ 0·8494, $d_{4^\circ}^{61{\cdot}0^\circ}$ 0·8321, $d_{4^\circ}^{85{\cdot}5^\circ}$ 0·8106. Apparatus *D*.

15·6°	13·72	0·8713	29·52	284·0	60·9	12·00	0·8322	24·66	284·3
22·1	13·55	0·8657	28·97	284·5	85·4	11·11	0·8107	22·44	284·4
40·5	12·80	0·8498	26·86	284·4				Mean	284·3

119. *n-Propylbenzene. Method* I.—This was prepared from benzyl chloride, b. p. 177—179°/757 mm., magnesium, and purified ethyl sulphate according to *Org. Synth.*, Coll. Vol. I, 1932, 458, with the modification that the crude product (100 g.), after drying over potassium hydroxide pellets, was distilled from sodium through a lagged three-section Pyrex Young and Thomas fractionating column; 60 g. of *n*-propylbenzene, b. p. 156—158°/756 mm., were obtained and there was a considerable residue in the flask. Upon redistillation from sodium, this boiled largely at 158—158·5°/771 mm. and a middle fraction had $d_{4^\circ}^{20^\circ}$ 0·8649, $n_D^{20^\circ}$ 1·49338. The resulting hydrocarbon was washed with 8-ml. portions of concentrated sulphuric acid until the acid layer was colourless (3 washings), and the pure *n*-propylbenzene isolated as under toluene.

B. p. 158·5°/760 mm.; M 120·19; n_C 1·48904, n_D 1·49313, n_F 1·50283, $n_{G'}$ 1·51194; R_C 40·13, R_D 40·42, R_F 41·09, $R_{G'}$ 41·72; $Mn_D^{20^\circ}$ 179·46. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8643, $d_{4^\circ}^{40{\cdot}5^\circ}$ 0·8473, $d_{4^\circ}^{60{\cdot}4^\circ}$ 0·8310, $d_{4^\circ}^{84{\cdot}6^\circ}$ 0·8109. Apparatus *A*.

15·1°	18·26	0·8684	29·69	323·1	59·7	16·12	0·8316	25·10	323·5
22·5	17·97	0·8622	29·01	323·5	85·3	14·82	0·8103	22·49	323·0
41·3	16·99	0·8463	26·92	323·5				Mean	323·3

Method 2. 100 G. of propiophenone (XI, **139**), reduced as for toluene, afforded, after steam distillation, 64 g. of crude *n*-propylbenzene; the viscid liquid residue in the flask probably consisted largely of phenylethylcarbinol. Upon redistillation from sodium through a Pyrex Young and Thomas column about 90% distilled at 160—165°/764 mm. (mainly at 160—162°) and evidently contained an appreciable quantity of an unsaturated hydrocarbon (allyl- and/or propenyl-benzene). This was washed with 10% of its volume of concentrated sulphuric acid until the acid layer was colourless (at least 10 washings; loss about 30%) and the pure hydrocarbon was isolated as under toluene.

B. p. 157·5°/763 mm.; *M* 120·19; n_{C} 1·48805, n_{D} 1·49215, n_{F} 1·50243, $n_{\mathrm{G'}}$ 1·51070; R_{C} 40·21, R_{D} 40·50, R_{F} 41·21, $R_{\mathrm{G'}}$ 41·78; $Mn_{\mathrm{D}}^{20^\circ}$ 179·35. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8613, $d_{4^\circ}^{42\cdot0^\circ}$ 0·8434, $d_{4^\circ}^{60\cdot6^\circ}$ 0·8282, $d_{4^\circ}^{86\cdot0^\circ}$ 0·8072. Apparatus *D*.

t.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
16·9°	13·63	0·8638	29·08	323·5	60·6°	12·04	0·8282	24·63	323·6
23·6	13·33	0·8584	28·26	323·2	85·9	11·13	0·8073	22·19	323·5
41·2	12·66	0·8440	26·39	323·1				Mean	323·4

Method 3. 75 G. of benzyl methyl ketone (XI, **132**), reduced with amalgamated zinc and concentrated hydrochloric acid, afforded, after steam distillation, 48 g. of the organic product. Upon distillation from sodium, 38 g. of crude *n*-propylbenzene, b. p. 157—162°/770 mm., were obtained; unsaturated hydrocarbons were removed by 20 washings with 4-ml. portions of concentrated sulphuric acid and the pure hydrocarbon was isolated as usual.

B. p. 157·5°/763 mm.; *M* 120·19; n_{C} 1·48769, n_{D} 1·49174, n_{F} 1·50208, $n_{\mathrm{G'}}$ 1·51042; R_{C} 40·15, R_{D} 40·43, R_{F} 41·16, $R_{\mathrm{G'}}$ 41·73; $Mn_{\mathrm{D}}^{20^\circ}$ 179·29. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8620, $d_{4^\circ}^{41\cdot2^\circ}$ 0·8444, $d_{4^\circ}^{61\cdot5^\circ}$ 0·8280, $d_{4^\circ}^{85\cdot7^\circ}$ 0·8079. Apparatus *A*.

17·1°	18·07	0·8644	29·25	323·4	61·8°	15·87	0·8278	24·60	323·4
20·8	17·80	0·8614	28·71	323·0	86·9	14·62	0·8069	22·09	323·0
41·1	16·82	0·8445	26·60	323·2				Mean	323·2

120. iso*Propylbenzene*.—The unsaturated hydrocarbons present in 100 g. of a pure commercial sample were removed by washing 5 times with 10-ml. volumes of concentrated sulphuric acid, the product was washed successively with water, 10% sodium carbonate solution, and water, and dried ($MgSO_4$); it was then fractioned over sodium through a three-section Pyrex Young and Thomas column and the fraction (*ca*. 90%), b. p. 151—152°/760 mm., was collected. This was again distilled over sodium, and a middle fraction collected for the physical measurements.

B. p. 151°/758 mm.; *M* 120·19; n_{C} 1·48684, n_{D} 1·49088, n_{F} 1·50110, $n_{\mathrm{G'}}$ 1·50931; R_{C} 40·11, R_{D} 40·39, R_{F} 41·10, $R_{\mathrm{G'}}$ 41·67; $Mn_{\mathrm{D}}^{20^\circ}$ 179·19. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8616, $d_{4^\circ}^{41\cdot2^\circ}$ 0·8442, $d_{4^\circ}^{61\cdot2^\circ}$ 0·8274, $d_{4^\circ}^{86\cdot7^\circ}$ 0·8058. Apparatus *D*.

13·9°	13·38	0·8667	28·64	320·8	60·9°	11·64	0·8276	23·79	320·7
41·2	12·35	0·8442	25·75	320·7	86·3	10·81	0·8061	21·52	321·1
								Mean	320·8

121. n-*Butylbenzene*.—*Method* 1. 75 G. of butyrophenone, b. p. 227—230°/777 mm. (XI, **140**), were reduced with 150 g. of amalgamated zinc and concentrated hydrochloric acid and yielded, upon steam distillation, 50 g. of an organic product. The crude *n*-butylbenzene, b. p. 181—184°, isolated by distillation from sodium was washed with 7-ml. portions of concentrated sulphuric acid until the acid layer was colourless, and the pure hydrocarbon was isolated as under toluene.

B. p. 181·5°/767 mm.; *M* 134·21; n_{C} 1·48577, n_{D} 1·48960, n_{F} 1·49948, $n_{\mathrm{G'}}$ 1·50743; R_{C} 44·81, R_{D} 45·11, R_{F} 45·88, $R_{\mathrm{G'}}$ 46·50; $Mn_{\mathrm{D}}^{20^\circ}$ 199·92. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8595, $d_{4^\circ}^{41\cdot0^\circ}$ 0·8444, $d_{4^\circ}^{61\cdot6^\circ}$ 0·8281, $d_{4^\circ}^{87\cdot3^\circ}$ 0·8081. Apparatus *D*.

18·5°	13·71	0·8606	29·14	362·3	61·0°	12·21	0·8286	24·99	362·1
24·1	13·58	0·8564	28·72	362·8	87·1	11·43	0·8083	22·82	362·9
41·5	12·88	0·8440	26·85	362·0				Mean	362·4

Method 2. 70 G. of benzyl ethyl ketone, b. p. 113—115°/17 mm. (XI, **133**), were reduced as in the preceding preparation. The crude *n*-butylbenzene, b. p. 180—183°/760 mm., isolated by steam distillation (62 g.) and distillation from sodium, weighed 50 g. This was washed 10 times with 10-ml. portions of concentrated sulphuric acid, and the pure hydrocarbon was obtained after two distillations over sodium in the usual manner.

B. p. 180·5—181°/767 mm.; *M* 134·21; n_{C} 1·48567, n_{D} 1·48955, n_{F} 1·49942, $n_{\mathrm{G'}}$ 1·50738; R_{C} 44·78, R_{D} 45·08, R_{F} 45·85, $R_{\mathrm{G'}}$ 46·47; $Mn_{\mathrm{D}}^{20^\circ}$ 199·92. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8601, $d_{4^\circ}^{41\cdot0^\circ}$ 0·8442, $d_{4^\circ}^{61\cdot2^\circ}$ 0·8283, $d_{4^\circ}^{86\cdot5^\circ}$ 0·8083. Apparatus *A*.

13·6°	18·34	0·8651	29·71	362·2	41·0°	16·98	0·8442	26·84	361·9
20·0	17·99	0·8601	28·97	362·0	60·9	16·01	0·8285	24·84	361·8
25·4	17·76	0·8559	28·46	362·2	87·3	14·85	0·8076	22·46	361·8
								Mean	362·0

122. n-*Amylbenzene*.—*Method* 1. 36 G. of valerophenone, b. p. 104—106°/5 mm., prepared by the reactions

$$\begin{array}{c} n\text{-Valeric acid} \\ \text{(Eastman Kodak)} \end{array} \xrightarrow{SOCl_2} \begin{array}{c} n\text{-Valeryl chloride} \\ \text{(b. p. 125—127°/758 mm.)} \end{array} \xrightarrow[\text{(excess)}]{AlCl_3;\ C_6H_6} \text{Valerophenone}$$

were reduced with 100 g. of amalgamated zinc and concentrated hydrochloric acid. The mixture was steam distilled, and the organic layer (19 g.) was distilled from sodium to give 16 g. of crude *n*-amylbenzene, b. p. 199—203°/768 mm. (mainly 201—202°). This was washed 10 times with 3-ml. portions of concentrated sulphuric acid, and the pure hydrocarbon was isolated as usual after two distillations from sodium.

B. p. 203°/774 mm.; M 148·24; n_{C} 1·48478, n_{D} 1·48849, n_{F} 1·49802, $n_{\mathrm{G'}}$ 1·50523; R_{C} 49·42, R_{D} 49·76, R_{F} 50·56, $R_{\mathrm{G'}}$ 51·18; $Mn_{\mathrm{D}}^{20^\circ}$ 220·68. Densities determined: $d_{4^\circ}^{20}$ 0·8594, $d_{4^\circ}^{41\cdot6^\circ}$ 0·8440, $d_{4^\circ}^{59\cdot5^\circ}$ 0·8306, $d_{4^\circ}^{87\cdot6^\circ}$ 0·8091. Apparatus *D*.

t.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
18·4°	13·89	0·8606	29·52	401·5	61·3	12·50	0·8296	25·61	402·0
25·2	13·72	0·8556	28·99	402·0	87·4	11·62	0·8092	23·22	402·1
41·7	13·15	0·8439	27·41	401·9				Mean	401·9

Method 2. 70 G. of benzyl *n*-propyl ketone, b. p. 243—247°/757 mm. (XI, **134**), were reduced with 160 g. of amalgamated zinc and concentrated hydrochloric acid. Steam distillation afforded 64 g. of an organic liquid which, upon distillation from sodium, yielded 60 g. of crude *n*-amylbenzene, b. p. 197—205° (mainly 201—203°). This was washed 11 times with 10-ml. portions of concentrated sulphuric acid and yielded, after two distillations over sodium, as usual, 40 g. of the pure hydrocarbon.

B. p. 202·5°/774 mm.; M 148·24; n_{C} 1·48459, n_{D} 148835, n_{F} 1·49796, $n_{\mathrm{G'}}$ 1·50552; R_{C} 49·40, R_{D} 49·73, R_{F} 50·56, $R_{\mathrm{G'}}$ 51·21; $Mn_{\mathrm{D}}^{20^\circ}$ 220·64. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8593, $d_{4^\circ}^{41\cdot2^\circ}$ 0·8438, $d_{4^\circ}^{61\cdot5^\circ}$ 0·8286, $d_{4^\circ}^{86\cdot5^\circ}$ 0·8098. Apparatus *D*.

13·2°	14·14	0·8643	30·18	402·0	41·1°	13·17	0·8439	27·45	402·1
19·9	13·88	0·8594	29·46	401·8	61·1	12·51	0·8289	25·61	402·3
24·4	13·74	0·8560	29·05	402·0	87·2	11·58	0·8093	23·15	401·8
								Mean	402·0

123. n-*Hexylbenzene*.—94 G. of 2-phenylethyl *n*-propyl ketone, b. p. 140—143°/17 mm. (XI, **137**), were reduced as in the last preparation. Steam distillation afforded 82 g. of an organic product which, when distilled over sodium, gave 54 g. of crude *n*-hexylbenzene, b. p. 218—230°, and 18 g. of a fraction, b. p. 230—240°, which was not investigated. The crude hydrocarbon was washed 15 times with 5-ml. portions of concentrated sulphuric acid and the pure *n*-hexylbenzene was isolated in the usual manner after two distillations over sodium.

B. p. 222·5°/766 mm.; M 162·26; n_{C} 1·48375, n_{D} 1·48739, n_{F} 1·49652, $n_{\mathrm{G'}}$ 1·50399; R_{C} 53·95, R_{D} 54·29, R_{F} 55·15, $R_{\mathrm{G'}}$ 55·86; $Mn_{\mathrm{D}}^{20^\circ}$ 241·35. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8602, $d_{4^\circ}^{42\cdot0^\circ}$ 0·8441, $d_{4^\circ}^{62\cdot8^\circ}$ 0·8292, $d_{4^\circ}^{86\cdot5^\circ}$ 0·8116. Apparatus *A*.

19·8°	18·56	0·8603	29·90	441·0	60·5°	16·76	0·8309	26·08	441·3
24·1	18·37	0·8572	29·79	442·2	86·0	15·62	0·8120	23·75	441·1
40·1	17·74	0·8455	28·09	441·8				Mean	441·5

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