956. *The Molecular Configuration of Liquid* n-*Aliphatic Homologues.*

By S. A. Mumford.

A critical review of the literature indicates that certain of the physical parameters of the liquid *n*-alkanes exhibit a marked discontinuity in the vicinity of the C_{16} term, the magnitude of functions depending primarily on intermolecular forces (*e.g.*, those derived from viscosity, vapour pressure, etc.) being less, and that of molecular volume functions greater, for the higher members of the series, than would be estimated by extrapolation from the data for the lower terms. This discontinuity is correlated with the intersection of the α-f. p. and β-m. p. curves which occurs in the same region, and it is shown that whilst the lower liquid alkanes, with " normal " molecular volume and intermolecular force increments, crystallise or tend to crystallise initially in the " tilted "-chain β-form, those above C_{16}, with larger molecular volume and smaller intermolecular force increments, set to the vertical-chain α-form, in which the molecules occupy a larger cross-sectional area and have greater mobility.

This and other evidence is interpreted as indicating that whilst the molecules in the higher liquid alkanes have an α-(*trans*-)configuration, and consist of rigid rotating planar zig-zag CH_2 chains as in the α-crystals to which they set, those in the lower liquid alkanes have a helical β-(approx. *cis*-)-configuration, derived by rotating each C–C link of the α-chain through an angle of 56° to the *trans*-position, the helix uncoiling on crystallisation to give the " tilted "-chain β-crystals. Such a difference in configuration is shown to be capable of accounting for the difference between the lower and higher alkanes in respect of variation of physical properties with chain length.

Extension of similar ideas to other liquid aliphatic homologues is shown to be consistent with the viscosity and freezing-point data available.

The implications of the basic hypothesis are briefly discussed in the light of current views on liquid structure.

In considering the physical properties of liquid aliphatic homologues, it is customary to assume that, after initial irregularities, accepted as inevitable " first-term anomalies," the properties under standard conditions of succeeding members of a series vary progressively and regularly with increase in chain length. Graphical demonstration that the properties of a particular compound fall on smooth curves drawn through those of its lower and higher homologues has, indeed, been commonly used as a check on the purity of compounds, and some ingenuity has been expended in developing equations to reproduce the variation of certain such properties with chain length. When, however, large-scale plots of this variation are made from the most reliable data, it is difficult to avoid the conclusion that the curves obtained are not, in some instances, continuous, but appear to be made up of two not quite coincident curves superimposed upon one another and intersecting in the vicinity of the C_{16} term. Systematic examination of the matter shows that the corresponding curves for a number of derived functions, particularly those depending on intermolecular forces, exhibit an even more marked change in direction at or about C_{16}, and the primary purpose of this paper is to review briefly the evidence pointing to the existence of such a discontinuity in the *n*-alkane series, and to examine its implications from the point of view of molecular structure.

As far as practicable, the functions selected for examination have been those which, for the lower members of the series, are known to vary approximately linearly with increasing chain length. It has therefore been possible to draw the graphs illustrating the discontinuity in this variation as pairs of intersecting straight lines, though it is appreciated that on general theoretical grounds rigorous linearity throughout is not to be expected, and that the change in slope will probably take place over a range of terms rather than at a " point of intersection." The paucity and scatter of the data for the higher alkanes, moreover, make it difficult in certain instances to locate the latter "point" with any precision, but since the balance of evidence indicates that the change in slope occurs at or close to C_{16}, it is referred to below as the "hexadecyl discontinuity," and the figures have been drawn on this basis throughout.

The Hexadecyl Discontinuity in the n-*Alkane Series.*

Intermolecular Force Functions.—Viscosity is one of the more important properties depending on the intermolecular forces in liquids. For normal liquids the variation of dynamic viscosity (η) with temperature ($T°$ K) is, to a first approximation, expressible by an equation of the Arrhenius type:

$$\log \eta = B/T - A \qquad (1)$$

When $\log \eta$ is plotted against $1/T$ for the various *n*-paraffins, a series of approximately straight lines, of gradually increasing slope, is obtained, and from an examination of the equations fitting these lines Linke (*Z. physikal. Chem.*, 1940, **187**, *A*, 227) and Kierstead and Turkevich (*J. Chem. Phys.*, 1944, **12**, 24) concluded that the constants A and B were linear functions of the chain length (cf. also the considerations advanced by Pospekhov, *J. Appl. Chem., U.S.S.R.*, 1950, **23**, 170).

The data employed by these authors, were, however, confined for the most part to alkanes below C_{16}. More recently, measurements have been reported of the viscosities of a number of higher paraffins by Schmidt, Schoeller, and Eberlein (*Ber.*, 1941, **74**, 1313), Schiessler *et al.* (*Proc. Amer. Petrol. Inst.*, 1946, **26**, III, 254), Nederbragt and Boelhouwer (*Physica*, 1947, **13**, 305), Mazee (*Rec. Trav. chim.*, 1948, **67**, 197), and Doolittle and Paterson (*J. Amer. Chem. Soc.*, 1951, **73**, 2145). Values have been calculated from these for the constants A and B over the temperature range 20° (or m. p., whichever is higher) to 100°, and these, together with similarly calculated constants from previously available data, have been plotted against n, the number of carbon atoms in the chain, in Fig. 1*a*. The plot appears to indicate unequivocally that the approximate linearity of the variation exhibits in both cases a sharp discontinuity at the C_{16} term. Below this point the increments per carbon atom of the constants A and B are 0·042 and 43, whereas above it they drop to 0·012 and 19·5, respectively. For a given paraffin both constants vary somewhat according to the temperature range considered, particularly in the vicinity of the freezing point, and the change in slope in Fig. 1*a* may be due in part to the smaller and higher temperature range covered with the higher paraffins. Such variations, however, do not of themselves account for the discontinuity: it persists when values calculated from the uniform and restricted temperature range of 70—90° are employed, and is indeed even more marked when the data of Nederbragt and Boelhouwer and of Doolittle and Paterson for hydrocarbons above C_{16} are used for calculation of the constants over temperature ranges as wide and as far removed from the relevant melting points as is 20—100° in the case of the lower paraffins.

In an analogous plot, from somewhat limited data, of dH, the heat of activation for viscous flow calculated from the slope of the $(\log \eta)$–$1/T$ line, Kauzmann and Eyring (*J. Amer. Chem. Soc.*, 1940, **62**, 3113; cf. Barrer, *Trans. Faraday Soc.*, 1943, **39**, 48) drew a continuous curve showing concavity towards the *n*-axis, and interpreted this apparent trend towards a limiting value as supporting the view that viscous flow took place by chain segments, the heat of activation tending to a maximum value when these comprised 20—25 atoms. It seems evident from Fig. 1*a*, however, that the curve is discontinuous and made up of two intersecting approximately linear portions, so that any interpretation based on assumed continuity would appear to be of doubtful validity.

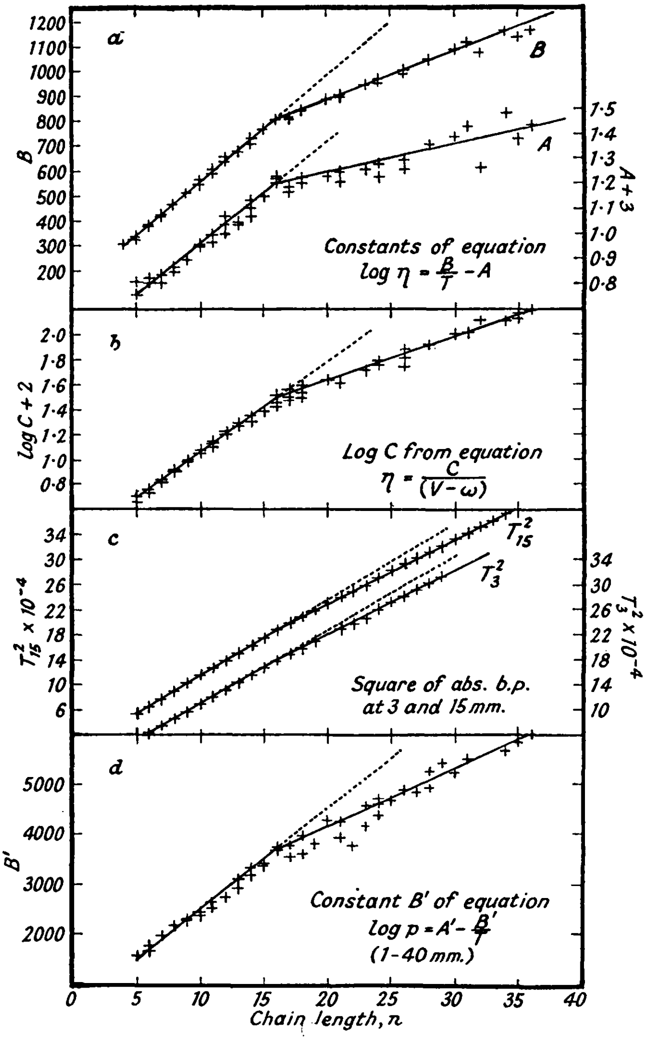
Similar evidence of discontinuity is afforded by the variation of the parameter C of Batchinski's equation (*Z. physikal. Chem.*, 1913, **84**, 643) relating viscosity to free space:

$$\eta = C/(V - \omega) \qquad (2)$$

in which η and V are the viscosity and molecular volume respectively of a liquid at a given temperature, and C and ω are constants, the former being considered by Batchinski to be related to the attraction constant $\sqrt{a}$, and the latter, the limiting molecular volume, to the volume b, of the van der Waals equation of state. Values of C have been calculated from available data for the n-paraffins. A plot of log C against n (Fig. 1b) resembles the B–n plot in consisting of two approximately straight lines intersecting at about C_{16}, the slope being 0·074 per carbon atom below, and 0·036 per carbon atom above, this point.

It being borne in mind that B in equation (1) and log C in equation (2) are measures of the strength of the intermolecular field, the conclusion appears inevitable that the molecules

FIG. 1. *Intermolecular force functions in* n-*alkane series: viscosity and vapour-pressure functions.*



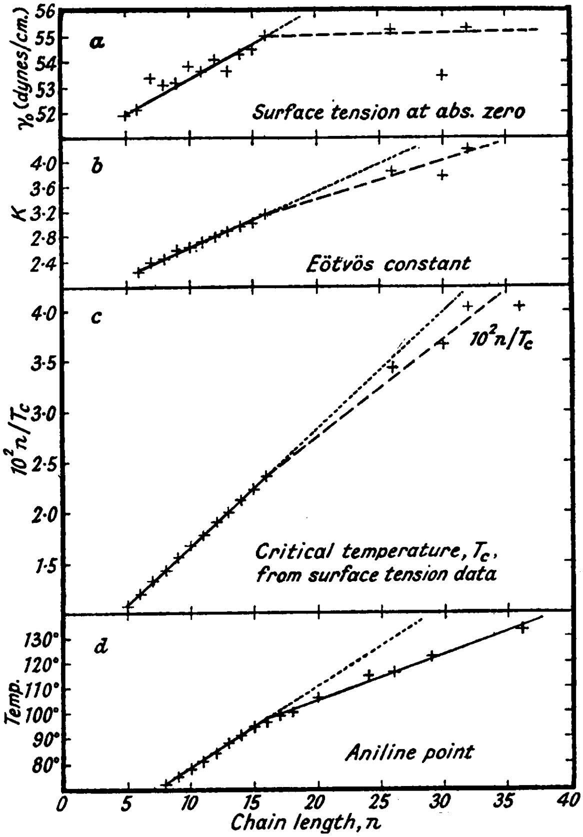
of the higher members of the series are subjected to smaller intermolecular forces than would be estimated by extrapolation from the values for lower members.

If this is so, other functions depending primarily on intermolecular forces should exhibit an analogous discontinuity, and in view of the known parallelism between fluidity and volatility, it would be expected that the vapour pressures of the higher liquid paraffins would be greater, and their boiling points under a given pressure (T_b° K) correspondingly lower, than estimated by extrapolation. To examine this point, use has been made of the linear relation

$$T_b^2 = an + b \qquad (3)$$

originally put forward by Boggio-Lera (*Gazzetta*, 1899, **29**, 441) and shown to hold for aliphatic series in general by Aten (*J. Chem. Phys.*, 1937, **5**, 260 : cf. also the " Siedezahlen " of Klages, *Ber.*, 1943, **76**, 788). Data for the boiling points of the *n*-paraffins at 3 and 15 mm. pressure taken from Stull's compilation (*Ind. Eng. Chem.*, 1947, **39**, 517) and supplemented by the more recent data of Mazee and Schiessler *et al.* for higher alkanes have been plotted on this basis in Fig. 1*c*. It is apparent that both lines show a discontinuity at about C_{16}, the boiling points of higher members of the series increasing more slowly with increasing chain length than do those of the lower members.

FIG. 2. *Intermolecular force functions in* n-*alkane series*: *surface-tension, etc., functions.*



The intimate connection between heat of activation for viscous flow and heat of vaporisation (cf. Eyring, *loc. cit.*; Nissan, Clark, and Nash, *J. Inst. Petrol.*, 1940, **26**, 155) makes it probable that the discontinuity noted above with the former would be apparent also with the latter. Estimation of heat of vaporisation in the usual way from the two-term equation

$$\log p = A' - B'/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where p is the vapour pressure (in mm.) at $T°$ K, involves in effect determination of the slope of the $(\log p)$–$1/T$ plot. Any such differentially deduced function is necessarily very susceptible to inaccuracies in the experimental observations, and in the present connection these may be considerable if a simple distillation technique is employed. Some scatter of data is therefore to be expected, and is in fact apparent in the B' values which have been calculated from the observations recorded in the literature for the boiling points of the *n*-paraffins over the pressure range 1—40 mm. Nevertheless, a plot of these values against chain length (Fig. 1*d*) shows close similarity to the corresponding B–n curve, the points for terms above C_{16} falling progressively below the line drawn through those for lower members of the series.

A further property depending ultimately on intermolecular forces is surface tension, and in conformity with the general picture presented above, the values of the surface tension of the *n*-alkanes at 70° (cf. Vogel, *J.*, 1946, 133) when plotted against log $(n - 3)$ following Wiener's empirical relation (*J. Phys. Chem.*, 1948, **52**, 1082) give a straight line up to $n = 16$, while the few available points for higher members, C_{26} and C_{60} (Schenck and Kintzinger, *Rec. Trav. chim.*, 1923, **42**, 759), C_{30} (Adam, *Phil. Mag.*, 1929, **8**, 539), C_{32} (Hunten and Maass, *J. Amer. Chem. Soc.*, 1929, **51**, 153), and C_{36} (Waterman, Leendertse, and van Krevelen, *J. Inst. Petrol.*, 1939, **25**, 801) fall progressively below this line (curve not reproduced).

So too with γ_0, the surface tension at absolute zero in the equation

$$\gamma = \gamma_0 (1 - T/T_c)^{1\cdot2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which has been shown by Ferguson (*Phil. Mag.*, 1916, **31**, 37; cf. *Trans. Faraday Soc.*, 1936, **32**, 1474) and Sugden (*J.*, 1924, **125**, 32) to express the variation of surface tension over a wide temperature range, and also with the constant K in the well-known Eötvös–Ramsay–Shields equation:

$$\gamma V^{2/3} = K(T_c - T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which γ is the surface tension and V the molecular volume at T° K, and T_c is the critical temperature.

The mean values of γ_0, interpreted by Sugden (*J.*, 1924, **125**, 1167) as measures of the total surface energies of different liquids at corresponding temperatures, have been plotted against n in Fig. 2*a*, from which, despite the scatter and paucity of the data, it would appear that the approximately linear increase of γ_0 with n is not maintained above $n = 16$.

The values of K, plotted against n (Fig. 2*b*), show a similar discontinuity at C_{16}. From C_5 to C_{16}, K increases with chain length according to the equation

$$K = 2{\cdot}135 + 0{\cdot}091(n - 5) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

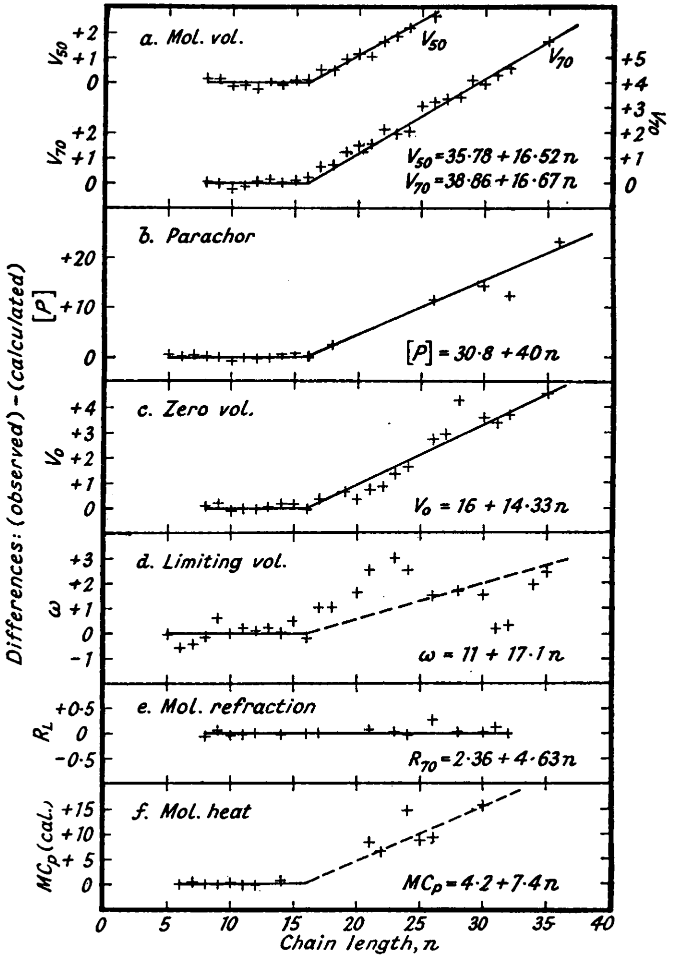
but the values for higher members are lower than would be estimated by extrapolation of this line. The approximate constancy of the Eötvös constant K at 2·12, originally postulated from measurements on a limited number of normal liquids of comparatively low molecular weight, has long been accepted as being without general significance (cf. Bennett, *J.*, 1924, **125**, 958), and many instances of higher values for liquids of greater molecular weight have been recorded. Assuming surface orientation of molecules, Adam (*loc. cit.*) indicated that with increasing chain length K will increase with $x^{2/3}$, where x is the ratio of molecular length to cross-section. On this basis, the decrease above C_{16} of the increment of K per carbon atom would connote a smaller chain-length increment, and/or a larger molecular cross-section above this point.

The values for the critical temperature T_c estimated by means of equations (5) and (6) are in general agreement despite their independent differential deduction. A plot of the mean T_c values against n gives a curve of shape suggesting linearity between $1/T_c$ and $1/n$, and this has been confirmed by plotting $10^2n/T_c$ against n (Fig. 2*c*). Here again, the linearity of the plot does not extend to terms above C_{16}, the $10^2n/T_c$ values for which are low. For these terms, therefore, the calculated T_c values are higher than would be expected by extrapolation. This, in effect, has been noted previously by Katz and Saltman (*Ind. Eng. Chem.*, 1939, **31**, 91), who found that a straight line was obtained by plotting values of γ against T/T_c for the *n*-alkane series, but that the points for C_{26}, C_{32}, and C_{60} fell well below this line. This they attributed either to a decrease of γ in the case of these long-chain compounds, or to incorrect extrapolation of T_c.

For other properties of the alkanes depending primarily on intermolecular forces, the available data are not sufficiently extensive for a comprehensive survey to be made, but two further indications of discontinuity at C_{16} may be noted. First, Kemp and Peters's finding (*Ind. Eng. Chem.*, 1943, **35**, 1108) that the plot against chain length of the quotient log relative viscosity)/(concentration) for *n*-paraffin solutions in hexane and other solvents) is linear above C_{16} but deviates negatively below this point. Second, the circumstance that the aniline points reported by Schiessler *et al.* (*loc. cit.*; cf. also Tilucheev and Kachmarchik, *J. Gen. Chem. U.S.S.R.*, 1951, **21**, 78) for alkanes above hexadecane, when plotted against chain length, fall progressively below the line drawn through the values for the lower members of the series (Fig. 2*d*).

Molecular Volume Functions.—Since molecular volume includes both the volume actually occupied by the molecules, and a spatial envelope round each, the magnitude of which is determined by the intermolecular forces, the discontinuity noted above in functions depending primarily on the latter would be expected to be apparent also in molecular volume functions, though in the opposite direction and to a smaller extent, since, other things being equal, a considerable decrease in intermolecular forces will connote only a slight increase in intermolecular distance, and hence in apparent molecular volume. The molecular volume increment for alkanes above C_{16} would therefore be expected to be somewhat greater than for the lower members of the series, and this is in fact found to be the case.

FIG. 3. *Molecular volume functions in* n-*alkane series: differences between observed and calculated values.*



When the molecular volumes ($V = M/D$) of the *n*-alkanes at a given temperature are plotted against chain length, the curves appear to display slight convexity towards the *n*-axis—a circumstance reflected in the attempts which have been made to derive quadratic equations of the type $V = a + bn + c/n$ to fit. Except for the early terms, however, where high vapour pressures introduce complications, the observed molecular volumes are linear with *n* up to C_{16} according to the equations

$$\left.\begin{aligned} V_{50} &= 35{\cdot}78 + 16{\cdot}52n \\ V_{70} &= 38{\cdot}86 + 16{\cdot}67n \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

but the values for higher members of the series lie progressively above these lines and fit equations of steeper slope :

$$\left.\begin{aligned} V_{50} &= 32{\cdot}35 + 16{\cdot}75n \\ V_{70} &= 35{\cdot}42 + 16{\cdot}91n \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This is clearly shown in Fig. 3*a*, in which the differences *V* (observed) minus *V* (calculated from equations 8) are plotted against *n*, the lines showing definite discontinuity at about C_{16}.

Similar evidence is afforded by the parachor, $[P] = M\gamma^{1/4}/(D - d)$, which is interpreted by Sugden (*J.*, 1924, **125**, 1177) as a measure of molecular volume under conditions of similar internal pressure. The circumstance that the observed parachors of long-chain compounds are greater than predicted by summation of atomic and structural constants derived from short-chain compounds has long been recognised, and is exemplified by the somewhat meagre data available for the higher alkanes. The CH_2 increment does not, however, increase progressively with chain length (cf. Gibling, *J.*, 1941, 299, 304) but remains constant at 40 units up to C_{16}, above which point it increases to *ca.* 41·15 units. This discontinuity is evident from Fig. 3*b*, in which the differences [*P*] obs. minus [*P*] calc. from the constants given by Mumford and Phillips (*J.*, 1929, 2112; 1950, 75), *i.e.*, [*P*] calc. $= 30{\cdot}8 + 40n$, are plotted against chain length for the *n*-paraffin series.

The discontinuity is also apparent in molecular volume extrapolated to absolute zero, *i.e.*, Sugden's " zero volume " $V_0 = M/D_0$ (*J.*, 1927, 1786) derived from the relation

$$(D - d) = D_0(1 - T/T_c)^{0{\cdot}3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The best equation fitting mean values of V_0 calculated from available density data for the *n*-alkanes from C_8 to C_{16} is $V_0 = 16{\cdot}0 + 14{\cdot}33n$, whereas the values for higher members of the series, despite some scatter, lie consistently and progressively above this line (Fig. 3*c*).

With limiting volumes, ω, derived from Batchinski's viscosity relation (equation 2), the scatter of the mean values is greater and such that, while not inconsistent with the existence of a C_{16}-discontinuity, the values could be expressed within the limits of observational error by a single linear relation throughout (Fig. 3*d*).

Comparable data for refractive indices of the *n*-alkanes are somewhat meagre, but on using the n_D^{70} values observed by Muller and Pilat (*J. Inst. Petrol.*, 1935, **21**, 887), McKittrick, Henriques, and Wolff (*ibid.*, 1937, **23**, 616), Schmidt, Schoeller, and Eberlein (*loc. cit.*), and Mazee (*loc. cit.*) for the higher members of the series, and mean extrapolated literature values for the lower terms, molecular refractions, R_L, computed by the Lorentz–Lorenz formula, appear to be linear with chain length throughout the series (Fig. 3*e*). As R_L is fundamentally a measure of bond polarisability and not strictly a molecular volume, the absence of discontinuity is not, perhaps, unexpected.

From equations (8) and (9) it can be calculated that the coefficients of expansion between 50° and 70° of the higher liquid alkanes are progressively greater than would be estimated by extrapolation from the data for the lower members of the series. It would therefore be expected that their specific heats, C_p, over the same temperature range would be correspondingly greater, and this in fact appears to be the case from a comparison of the data of Garner, van Bibber, and King (*J.*, 1931, 1533), Spaght, Thomas, and Parks (*J. Phys. Chem.*, 1932, **36**, 882), and Mazee (*loc. cit.*) for a number of the higher alkanes, with values extrapolated from the observations of Parks *et al.* (*J. Amer. Chem. Soc.*, 1930, **52**, 1032; 1931, **53**, 3876) and Osborne and Ginnings (*J. Res. Nat. Bur. Stand.*, 1947, **39**, 453) for the lower members of the series. This is shown in Fig. 3*f*, in which the differences between observed molecular heats (50—70°) and values calculated from the equation $MC_p = 4{\cdot}2 + 7{\cdot}4n$ cal. are plotted against chain length.

The whole of the available evidence from the physical characteristics of the liquid *n*-alkanes would thus appear to be in accord with the inference that there is a discontinuity in properties in the vicinity of the C_{16} term, the molecules of higher members of the series being subjected to smaller intermolecular forces and occupying a larger volume than would be expected by extrapolation from the values for lower members.

The Freezing Points of the n-*Alkanes.*

A fundamental discontinuity of this nature would be expected to be reflected in some way in the freezing points of the liquid alkanes, and it does not seem unreasonable to connect it with the intersection of the α- and β-m. p. curves for the series, which occurs in approximately the same region (cf. Gray, *J. Inst. Petrol.*, 1943, **29**, 226; Phillips and Mumford, *J.*, 1934, 1657). The phase transformations of the paraffins are somewhat complex, but from the present aspect the salient features may be summarised as follows.

Both even and odd paraffins from C_{17} upwards crystallise, without supercooling (Mazee), in the soft, transparent α-form, which according to *X*-ray investigation consists of hexagonally-packed rotating planar zig-zag molecules with their axes vertical to the terminal planes (cf. Müller, *Proc. Roy. Soc.*, 1930, **127**, *A*, 417; 1932, **138**, *A*, 514). This form is metastable in the case of octadecane, and changes monotropically into a higher-melting opaque β-form on storage (Smith, *J.*, 1932, 737). With the C_{20} and C_{22} hydrocarbons the α-→ β-transition occurs a few degrees below the α-f. p. and has only been observed on cooling, though Seyer, Patterson, and Keays (*J. Amer. Chem. Soc.*, 1944, **66**, 179) note indications that the reverse transition takes place if the heating is slow enough. In the β-form the *X*-ray "long-spacing" is shorter than in the α-, ascribed to tilting of the axes of the CH_2 chains with respect to the terminal planes, and the molecules are non-rotating (Müller, *loc. cit.*; Piper *et al.*, *Biochem. J.*, 1931, **25**, 2072; cf. Müller and Lonsdale, *Acta Cryst.*, 1948, **1**, 129). The α-→ β-transition is accompanied by evolution of heat (Mazee) and contraction in volume (Seyer). The odd alkanes above C_{17} show no α-→ β-transition, the crystals exhibiting the vertical "long-spacing" down to liquid-air temperature. In common with the even members above C_{24}, however, they undergo reversible conversion a few degrees below the f. p. to an orthorhombic vertical non-rotating (α′) form (Müller).

The α-f. p.s, T_α° K, when plotted against chain length, *n*, lie on a smooth curve (Fig. 4*a*) to reproduce which various modifications of an equation of the type $T_\alpha(n + c) = an + b$ have been proposed, amongst them :

$T_\alpha = 396{\cdot}4 - 1659/(n - 1)$, *i.e.*, $T_\alpha(n - 1) = 396{\cdot}4n - 2055{\cdot}4$ (Gray, *loc. cit.*).

$T_\alpha = (0{\cdot}6085n - 1{\cdot}75)/(0{\cdot}001491n + 0{\cdot}00404)$, *i.e.*, $T_\alpha(n + 2{\cdot}71) = 408{\cdot}1n - 1174$ (Garner, van Bibber, and King, *loc. cit.*).

$T_\alpha = 414{\cdot}5M/(M + 94{\cdot}4)$, *i.e.*, $T_\alpha(n + 6{\cdot}88) = 414{\cdot}5n + 59{\cdot}7$ (Etassam and Sawyer, *J. Inst. Petrol.*, 1939, **25**, 253)].

$1/T_\alpha = 0{\cdot}002395 + 0{\cdot}0171/n$, *i.e.*, $T_\alpha(n + 7{\cdot}14) = 417{\cdot}5n$ (Mayer and van der Wyk, *Helv. Chim. Acta*, 1937, **20**, 1313)].

The first of these represents an attempt to deduce from theoretical considerations the variation of T_α with chain length, and the last two were derived from literature data for all the alkanes from C_{20} to C_{70}, and thus ignore the circumstance that from about C_{40} upwards the non-rotating α′-modification appears to be the stable form at the f. p. (cf. Gray; Müller; Seyer, *locc. cit.*). If the α-f. p.s for C_{17} to C_{40} alone are considered, as was done by Garner, the equation best fitting the most reliable recent data is

$$T_\alpha(n + 2{\cdot}5) = 404{\cdot}6n - 1129{\cdot}1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which reproduces the observed α-f. p.s of the *n*-alkanes from C_{17} to C_{40} to within ±0·3°.

At the lower end of the series, both odd and even paraffins from C_5 to C_8 crystallise, without supercooling (Shepard, Hanne, and Midgley, *J. Amer. Chem. Soc.*, 1931, **53**, 1948;

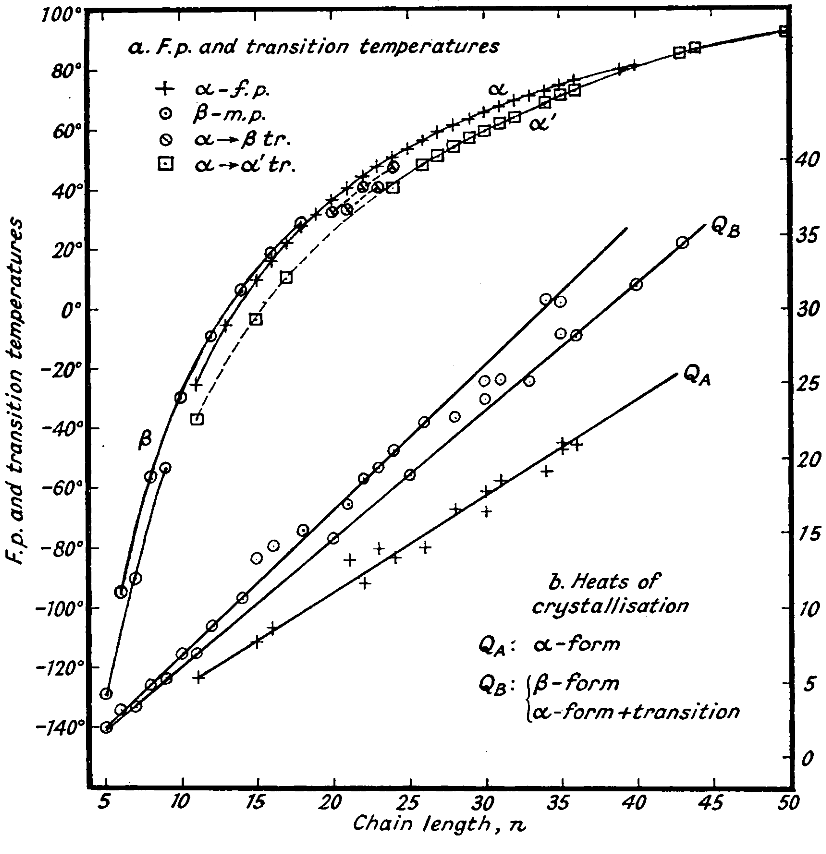
Smittenberg, Hoog, and Henkes, *ibid.*, 1938, **60**, 17), in the β-form, and the crystals show the "tilted" long-spacing down to the temperature of liquid air (Müller). The β-f. p.s (T_β° K) exhibit the alternation attributed by Malkin (*Nature*, 1931, **127**, 126) to the tilted-chain structure, those of the odd members being only slightly higher than those of the preceding even members. For the latter, the equation

$$T_\beta(n + 3{\cdot}4) = 398n - 719{\cdot}4 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

reproduces the β-f. p.s of *n*-hexane and octane, and the β-m. p. of *n*-octadecane.

As regards the *n*-alkanes between C_{17} and C_8, Smith (*loc. cit.*) found that *n*-hexadecane tends to crystallise in the α-form ($t_\alpha = 16{\cdot}2^\circ$) but that this is too unstable to exist except in the presence of a small amount of higher homologue, and the higher-melting β-modification ($t_\beta = 18{\cdot}13^\circ$) is normally obtained after slight supercooling. The observations that the crystals show no transition on cooling (Seyer) and exhibit only the shorter "long-spacing" (Müller) are in accord with this. The α-f. p. and β-m. p. are reproduced to within 0·2° by equations (11) and (12), respectively.

FIG. 4. *Temperatures and heats of crystallisation and transition* : n-*alkanes*.



With the C_{10}, C_{12}, and C_{14} hydrocarbons, according to the data of Mair (*J. Res. Nat. Bur. Stand.*, 1932, **9**, 457), Parks *et al.* (*J. Amer. Chem. Soc.*, 1931, **53**, 3876; 1934, **56**, 1511), Ubbelohde (*Trans. Faraday Soc.*, 1938, **34**, 282), and Schiessler *et al.* (*loc. cit.*), the respective setting and melting points are identical, and there is no evidence of supercooling, or of transition in the solid. The f. p.s are precisely reproduced by equation (12). It is clear that the crystalline form is the β-modification, and with *n*-decane this has been confirmed by *X*-ray examination (Müller).

Few data are available for the C_{11}, C_{13}, and C_{15} paraffins. The recorded m. p.s agree well with values calculated by equation (11), and for C_{11} and C_{15} Müller found that the crystals exhibited only the vertical " long-spacing " from room to liquid-air temperature. The endothermic transitions observed when the crystals are heated to within a few degrees of melting must therefore refer to the $\alpha' \rightarrow \alpha$-conversion. For C_{15} Ubbelohde records an f. p. somewhat lower than the m. p., and the same is generally true of recorded values for the other two, so that by analogy with the reverse phenomena in the case of C_{16} and C_{18}, it is possible that the C_{11}, C_{13}, and C_{15} liquids tend to set initially in the β-form, which, however, changes spontaneously to a higher-melting stable α-form.

With *n*-nonane, Parks (*loc. cit.*) recorded a transition just below the f. p., similar to that found with undecane, but the more recent work of Smittenberg *et al.* (*loc. cit.*) has not confirmed this. The latter find that it crystallises without supercooling, and that the f. p. and m. p. are identical. Since Müller observed only the shorter " long-spacing," it is clear that *n*-nonane normally crystallises in the β-form.

These data are plotted against chain length in Fig. 4*a*, from which it is evident that their explanation lies in the intersection of the α-f. p. curve with the odd β-m. p. curve in the vicinity of the C_9 term, and with the even β-m. p. curve about the C_{20} term. Below C_{15} the " tilted " chain β-form initially crystallises or tends to crystallise. This is stable with the even members, but with the odd is only stable up to C_9; from C_{11} to C_{15} it changes spontaneously to the higher-melting α-form. Above C_{16}, on the other hand, the reverse holds. The vertical, rotating chain α-form first crystallises out, and this is stable with the odd members : with the even, it is metastable with C_{16} and C_{18}, changing monotropically to the higher melting β-form, whilst in the case of C_{20} and C_{22} it is the stable form at the f. p. but undergoes a transition to the β-form a few degrees lower. With the odd paraffins from C_{11} upwards, and the even paraffins from C_{24} upwards, the position is complicated by the incidence of the vertical non-rotating α′-form into which the α-form changes enantiotropically a few degrees below the f. p.

In view of the known influence of rate of cooling and presence of impurity in retarding or inhibiting transitions in the solid state (see Smith, *loc. cit.*; Crowe and Smyth, *J. Amer. Chem. Soc.*, 1950, **72**, 1098; cf. also Müller's observation that with C_{18} and C_{20} both vertical and tilted spacings persist side by side from room to liquid-air temperature), it is not surprising that the data recorded for the heats of crystallisation and transition of the *n*-alkanes exhibit some scatter. They are nevertheless generally consistent with the conclusions drawn above, as is apparent from Fig. 4*b*, in which Q_A, the observed heats of crystallisation of the α-form of the higher alkanes, and Q_B, the observed heats of crystallisation of the β-crystallising lower alkanes (C_5 to C_8) and the total (Q_A plus heat of transition) for the higher alkanes, are plotted against chain length, in both instances giving approximately linear plots (a double plot, even > odd, in the case of Q_B). It will be seen that the heats of fusion recorded by Parks for C_{10}, C_{12}, and C_{14} fall on the Q_B (even) line, consistently with their β-structure. So also does the value given by Ubbelohde for the heat of fusion of pure hexadecane, though that of a less pure (and hence probaby α-crystallising) specimen falls on the Q_A line. For C_{11} and C_{15} the data of Parks and Ubbelohde respectively (in the latter case estimated from the specific-heat curve given in the paper) for the heats of fusion of the forms stable at the m. p. fall on the extrapolated Q_A line, whereas the total heats of fusion (*i.e.*, including heat of transition) lie near the Q_B line. The latter line is, of course, composite, since the included heat of transition refers in some cases to the $\alpha \rightarrow \beta$-, and in others to the $\alpha \rightarrow \alpha'$-transition. The circumstance that the precision of existing data is inadequate to differentiate between the two is of interest in indicating that the major process in both instances is the transition from rotating to non-rotating forms, and that the energy difference between the vertical and " tilted " chain structures *per se* is small in comparison.

The Configuration of n-*Alkane Chains.*

From the point of view of the hexadecyl discontinuity in physical properties, the most interesting and important aspect of the f. p. data considered in the preceding section is that, whereas the liquid alkanes below C_{16}, with " normal " molecular-volume and intermolecular-force increments, crystallise or tend to crystallise initially in the β-form, those above C_{16}, with their larger molecular-volume and smaller intermolecular-force increments, set to the α-form, in which the molecules occupy a larger cross-sectional area and have greater mobility (cf. King and Garner, *J.*, 1934, 1449; 1936, 1368). Assuming on the basis of modern theories that the liquid alkanes have a quasi-crystalline structure, with the axes of neighbouring molecules approximately parallel, and that the absence of supercooling implies that the structure of the liquid at the solidification point is fundamentally similar to that of the crystals initially produced, we infer that the inter- and intra-molecular arrangement in liquid paraffins above C_{16} must be essentially the same as that obtaining in α-crystals, but the same as that in β-crystals in the case of lower members of the series.

There is no difficulty about the first part of this inference. Müller, Seyer, and others have in fact indicated that the molecules in the higher liquid alkanes must be regarded as hexagonally-packed rigid zig-zag rotators as in the α-crystals, the difference between the two phases being that the molecules in the liquid are further apart and their terminal groups no longer in one plane. The latter part presents greater difficulty. On the basis of their shorter *X*-ray " long-spacing " and mono- or tri-clinic mode of crystallisation, it is generally accepted that in β-crystals the molecules are in the same planar zig-zag form, but with the chains non-rotating and their axes tilted with respect to the planes containing the terminal groups. It would be expected, however, that such a structure would melt to a liquid identical with the α-liquid postulated above, since non-rotation and tilt have no significance for molecules in the liquid phase. The alternative, as originally considered by Müller but rejected as unlikely, is to assume that the shortened " long-spacing " implies an alteration in chain structure involving a reduction in length as compared with the planar zig-zag arrangement. This would of course explain the *X*-ray observations on β-crystals, and the concomitant modification of cross-sectional dimensions and intramolecular arrangement could conceivably account for the different molecular-volume and intermolecular-force increments found in the β-liquids of the alkanes below C_{16}.

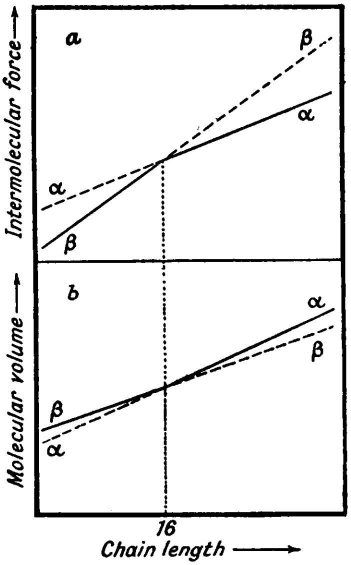


FIG. 5. *Relations of intermolecular forces and molecular volumes in α- and β-liquid alkanes.*

Continuous line = stable liquid form.

If this were so, it is clear from the evidence presented above that in the liquid phase the two chain configurations must be such as to satisfy the relations indicated in the idealised diagrams of Fig. 5, the intermolecular forces in the β-form being less in the case of small molecules, but increasing more rapidly with chain length, than in the α-, whilst the reverse holds for molecular volume.

The observed approximate linearity of both molecular volume and intermolecular force functions with chain length makes it probable that in the β-liquids, as in the α- : (i) One molecular species is predominantly present: it is unlikely that a mixture containing substantial proportions of different rotational isomers would have the same composition for all liquid alkanes below C_{15} over a range of temperatures. (ii) The molecules are linearly extended and approximately parallel: the molecular volume of coiled molecules resulting from free rotation about the carbon links would increase approximately as the 3/2 power of n (cf. Taylor, *J. Chem. Phys.*, 1948, **16**, 257). (iii) The carbon chain lengthens regularly: this excludes arrangements such as the sinusoidal  chain which would give alternating increments.

The simplest type of structure satisfying these conditions is one derived by twisting a zig-zag into a loose helix by rotation of each C–C link through an angle θ to the *trans*-position. It can be shown that with such a helix, each C–C link contributes an increment of length, l, along the axis given by

$$l^2 = L^2\left[1 - \frac{2\cos^2\alpha}{2 - \sin^2\alpha(1 - \cos\theta)}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and that the centre of each carbon atom is situated at a distance, r, from the axis given by

$$r = L\cos\alpha/[2 - \sin^2\alpha\,(1 - \cos\theta)] \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where L is the length of the C–C link (1·54 Å), and α is half the tetrahedral valency angle, *i.e.*, 54° 44′.

In the case of the planar zig-zag chain of the α-form, where $\theta = 0$, and therefore $(1 - \cos\theta) = 0$, these reduce to $l = L\sin\alpha = 1{\cdot}257$ Å, and $r = \frac{1}{2}L\cos\alpha = 0{\cdot}445$ Å. For the β-form, *X*-ray "long-spacing" data give a mean increment of 1·20 Å. The applicability of this to the molecules in β-liquids being assumed, substitution in equation (13) indicates that the angle of rotation required to form a helix having a length increment of this magnitude is about 56°, the proximity of which to 60°, the angle between the *trans*- and neighbouring *cis*-positions, may be significant.

In such a helix, the number of links, x, per revolution round the axis is given by

$$\cos 360/x = \sin^2\alpha(1 - \cos\theta) - 1 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

For the postulated β-helix, therefore, where $\theta = 56°$, $x = 2{\cdot}667 = 8/3$, *i.e.*, the helix repeats after 8 C–C links and 3 axial revolutions, the links, projected on to a plane normal to the axis, forming the 1 : 4 chords of a regular octahedron.

Each plane containing the centres of three successive carbon atoms in the helical chain is inclined at an angle ϕ to a plane normal to the axis given by $\sin\phi = l/(L\sin\alpha)$, so that for the β-helix, $\phi = 72° 40'$. This holds equally, of course, for the three end atoms of the helical chain, so that if the molecules of β-crystals were in such a form, Malkin's explanation of the alternation of long-spacing and of m. p. in such crystals as due to chain tilt would still apply.

Whether in fact the hydrocarbon chains in β-crystals have this helical structure seems doubtful in view of the crystallographic evidence. With the liquids, despite the similarity of the immediate environment of each carbon atom in the two types of chain, it would be expected that the difference between them would be indicated by precision molecular spectra measurements. So far as can be traced, however, few relevant observations appear to have been made, apart from that of Rosenbaum (*J. Chem. Phys.*, 1941, **9**, 295), who noted that in the Raman spectrum of liquid *n*-eicosane the low-lying lines (<800 cm.$^{-1}$) were few in number and diffuse, compared with those in the spectra of liquid octane, decane, and hexadecane. This, which he attributed to decrease in the number of co-existing rotational isomers, could presumably be equally indicative of a molecular configuration other than the *trans*-zig-zag one in the lower liquid alkanes. It is difficult, however, to account on this basis for the somewhat similar difference observed between the Raman spectra of the liquid and solid β-crystallising paraffins below C_{16}, which is again interpreted as indicating the presence of various rotational isomers in the liquids, but only one, presumed to be the *trans*-zig-zag form, in the solids (Okazaki, *J. Chem. Soc. Japan*, 1942, **63**, 1255, 1500; Sheppard and Szasz, *J. Chem. Phys.*, 1949, **17**, 86; Rank and Axford, *ibid.*, p. 430; cf. also Ubbelohde and McCoubrey, *Discuss. Faraday Soc.*, 1951, No. 10, 94).

If it is assumed that the latter is correct, and that the existence of a tilted planar zig-zag, as opposed to a helical, chain in β-alkane crystals is confirmed, it must be inferred from the evidence presented above that, whilst the molecules of the lower paraffins have a helical β-configuration in the liquid, this uncoils to a planar zig-zag on crystallisation. The inclination to the axis of the terminal 3-carbon group would then account for, and in fact determine, the tilt of the chain in the crystal. The circumstance that β-crystals show two unequal "side-spacings" on *X*-ray examination would appear to support this, for the non-rotating helical β-chain, unlike the non-rotating α-chain, would be symmetrical and expected to exhibit one "side-spacing" only.

The cross-sectional areas of the space occupied by the rotating α- and β-molecules in the liquid phase are not very different. From the molecular volume relation

$$(\text{Area in Å}^2)\ (\text{Length in Å}) \times 10^{-24} = \frac{(\text{Mol. wt.})}{\text{Density}} \times (\text{Mass of H atom, } i.e.,\ 1{\cdot}662 \times 10^{-24})$$

i.e.,

$$(\text{Area}) \times (\text{Length}) = 1{\cdot}662\ (\text{Mol. vol.}) \quad . \quad . \quad . \quad . \quad . \quad (16)$$

it is clear that for each carbon atom added

$$(\text{Area}) \times (\Delta\ \text{Length}) = 1{\cdot}662\ (\Delta\ \text{Mol. vol.}) \quad . \quad . \quad . \quad . \quad (17)$$

From the increments of chain length given above, and the molecular-volume increments given in equations (8) and (9), the cross-sectional areas occupied by the α- and β-forms at 50° C are therefore $1{\cdot}662 \times 16{\cdot}75/1{\cdot}257 = 22{\cdot}15$, and $1{\cdot}662 \times 16{\cdot}52/1{\cdot}202 = 22{\cdot}84$ Å², respectively. Parallel molecules hexagonally packed being assumed, the separation of the axes of neighbouring chains at 50° ($= \sqrt{2(\text{Area})/\sqrt{3}}$) is thus 5·057 and 5·136 Å in the two cases.

Warren (*Phys. Review*, 1933, **44**, 969) on this basis showed that Stewart's *X*-ray diffraction data (*ibid.*, 1928, **31**, 174) for the liquid *n*-paraffins from C_5 to C_{15} could be satisfactorily accounted for by assuming the planar zig-zag configuration, the main peak in the diffraction angle curves corresponding to a concentration of scattering matter at a distance approximating to the lateral distance between chain axes: compare also the similar deduction by Pierce (*J. Chem. Phys.*, 1935, **3**, 252) from Katzoff's data (*ibid.*, 1934, **2**, 841) for the *X*-ray scattering of liquid *n*-heptane. Consideration of this radial distribution method of calculation suggests, however, that if the molecules were in the helical β-configuration, the slight increase of interaxial distance involved and the concomitant re-arrangement of carbon atoms round the axes would not materially alter the calculated position of the "concentration of scattering matter" and hence of the diffraction peak. It seems doubtful, therefore, whether agreement between observation and calculation can be taken as evidence favouring one chain configuration in preference to another, but only as indicative of the presence of parallel and hexagonally-packed linearly extended molecules.

From the geometry of the generalised carbon chain discussed above, it can be shown that if the hydrogen atoms are attached at the tetrahedral angle, the distance, *s*, of the centres of the hydrogen atoms from the axis of the chain is given by

$$s^2 = (Hl/L)^2 + (r + H \cos \alpha)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where H is the length of the C–H link ($= 1{\cdot}09$ Å) and the other symbols are as previously used. This, on evaluation, gives $s = 1{\cdot}395$ for the α-, and 1·431 Å for the β-configuration. If, therefore, the radius of the hydrogen atom is taken as $(H - L/2) = 1{\cdot}09 - 0{\cdot}77 = 0{\cdot}32$ Å, the radii (R) of the cylinders of revolution of the α- and β-chains are 1·715 and 1·751 Å, and the cross-sections of these cylinders 9·24 and 9·632 Å², respectively. The volume increments per C–C link are thus $9{\cdot}24 \times 1{\cdot}257 = 11{\cdot}615$ Å³ for the α-, and $9{\cdot}632 \times 1{\cdot}202 = 11{\cdot}577$ Å³ for the β-chain.

So far as the ends of the alkane molecules are concerned, employment of H in place of L in equation (13) shows that the distance parallel to the chain axis from the centre of the terminal carbon atom to the centre of the attached terminal hydrogen atom is 0·89 Å in the case of the α-, and 0·851 Å in the β-chain; so that the axial distances, Y, from the terminal carbon atom centre to the outer surface of the end hydrogen atom (a radius of 0·32 Å being assumed for the latter) are 1·21 and 1·171 Å, respectively. The ends of the axially rotating molecules will thus approximate to segments of a sphere of radius R and height Y, and the volume of each will be $\pi Y(R^2 - Y^2/3)$, *i.e.*, 9·325 $Å^3$ for the α- and 9·598 $Å^3$ for the β-form.

The theoretical equations for the variation of dimensions with chain length in the two cases are therefore as follows :

	α-Form (planar zig-zag)	β-Form (octagonal helix)
Chain length, Å	$2{\cdot}42 + 1{\cdot}257(n - 1)$	$2{\cdot}342 + 1{\cdot}202(n - 1)$
Cross-section, $Å^2$, of rotating chain	$\pi \times 1{\cdot}715^2 = 9{\cdot}24$	$\pi \times 1{\cdot}751^2 = 9{\cdot}632$
Volume of rotating chain, $Å^3$	$18{\cdot}65 + 11{\cdot}615(n - 1)$	$19{\cdot}196 + 11{\cdot}577(n - 1)$

The volume equations are in full agreement with the observational requirement that the initial value should be higher and the increment less with the β- than with the α-form (see Fig. 5*b*). Simultaneous solution of the equations for the two forms indicates in fact that the lines intersect at $n = 15{\cdot}4$, as compared with the observed intersection in the vicinity of the C_{16} point. The agreement suggests that intramolecular configuration is closely bound up with spatial considerations, the molecules of the liquid *n*-paraffins adopting the α- or the β-configuration according to which possesses the greater volume.

Since the radii of the cross-sectional areas occupied by the axially rotating α- and β-molecules in the liquid phase are not very dissimilar, the marked difference in intermolecular-force increments noted above cannot be ascribed primarily to difference in molecular separation. In the case of the *n*-paraffins, these forces arise from the transient dipoles of the London dispersion effect, and might be expected to depend to some extent on the configuration of the chain, since this determines the relative positions of nuclei and electrons within the molecule. It may, therefore, be significant in this connection that the carbon atoms are nearer the outer surface of the rotating molecule in the β- (0·46 Å) than in the α-chain (0·5 Å). A small difference of this magnitude in the location of the transient dipoles within the molecule would appear to be of the right order to account for the observed difference of force strength at the surface; since the attractive force varies inversely as the 7th power of the distance (as indicated by differentiation of the London potential energy of interaction equation), the ratio of the intermolecular forces β : α would be $1/0{\cdot}46^7 : 1/0{\cdot}5^7 = 1{\cdot}8 : 1$, compared with the observed 2 : 1 ratio of the viscosity parameter increments. In addition, the force per C–C link would be concentrated over a somewhat smaller surface area ($= 2\pi Rl$) in the case of the rotating β-molecule (13·22 $Å^2$) than with the α- (13·55 $Å^2$).

Little can be said about the interactions at the ends of the molecules, but since the terminal planar area $[\pi(R^2 - Q^2)]$ over which the axial intermolecular force is spread is materially larger with the β-molecule (5·33 $Å^2$) than with the α- (4·64 $Å^2$), it might be expected that the terminal intermolecular forces would be less with the former. Qualitatively at least, therefore, the helical β-configuration would appear to be in accord with the observational requirement that the intermolecular forces are less in the case of small molecules, but increase more rapidly with chain length, with the β- than with the α-liquid alkanes (see Fig. 5*a*).

The energy relations between the α- and β-forms should be revealing, but the somewhat scanty data available do not permit of any detailed consideration of the matter. The heat evolved on transition from the α- to the β-form in the solid phase arises primarily, as indicated in the previous section, from cessation of rotation of the molecules in that phase, and affords no indication of the difference in energy content of the α- and β-configurations in the liquid phase. If this difference is of the low order estimated by Sheppard and Szasz (*loc. cit.*) for the energy difference between the rotational isomers inferred from Raman spectra in the lower liquid paraffins (*ca.* 500 cal./mol.), it is not surpising that the heat-capacity determinations by Parks and his co-workers (*loc. cit.*) led them to conclude that the molar entropies of the *n*-alkanes in the liquid state at 25° increased regularly with chain length from C_4 to C_{33}.

With alkanes in the vicinity of the discontinuity at C_{16}, the energy contents of the α- and β-liquids near the m. p. will clearly not be very different, and some interconversion of the two forms might be expected to occur in the liquid phase to give equilibrium mixtures of maximum entropy. The change in slope of the various parameter–chain length curves in this region will therefore tend to be in the nature of a gradual transition rather than a "point of intersection," as is indeed apparent from the data plotted in certain of the figures. In the case of the C_{11}, C_{13}, and C_{15} paraffins on the one hand, and the C_{16}, C_{18}, and C_{20} paraffins on the other, where, owing to the crossing of the α- and β-f. p. curves, the form stable in the solid at the m. p. differs from that stable in the liquid and in the initially setting solid, interconversion must occur either on melting or on subsequent heating of the melt. The observed temperature dependence of certain of the parameters of the liquid in the vicinity of the m. p. may be indicative of some interconversion taking place in the liquid phase, but the absence of any marked discontinuity suggests that the transition from one form to the other occurs mainly on melting, and that the relatively small energy change involved is unnoticeably included in the much greater heat of fusion.

With regard to the third ("*C*") modification observed by Piper *et al.* (*loc. cit.*) in *X*-ray examination of the even paraffins from C_{26} to C_{36}, this form, observed only in specimens prepared by crystallisation from solvents, is characterised by still shorter "long-spacings" than the β-, and hence presumably by larger tilt of the molecular axis. By extension of the hypothesis now presented, it seems possible that under certain conditions in the freer environment of solution, tighter coiling of the helical chain may occur. By analogy, the helix presumably uncoils on crystallisation from solution as on solidification from the liquid melt, though it may be noted that certain features of the optical properties of such crystals have been interpreted as indicating the presence in them of "spiral" chains (Hack, *Phys. Review*, 1937, **51**, 686; Hubbard, *Amer. Min.*, 1945, **30**, 645).

Other Homologous Series.

If the correlations noted in the preceding sections for the *n*-alkane series are valid, they must clearly be equally applicable, *mutatis mutandis*, to other homologous series of liquid aliphatic compounds. Data for the latter are somewhat meagre, but a preliminary survey appears to indicate that they are not inconsistent with the basic hypothesis advanced above. For such a survey, use has been made primarily of the intermolecular force parameter, log *C*, from equation (2), the approximately linear increments of which per CH_2 group in the *n*-alkane series have been shown above to change markedly in magnitude at about $n = 16$, corresponding with the change of chain configuration in the liquid phase ($\Delta \log C/\Delta n = 0{\cdot}036$ for α, $0{\cdot}074$ for β). The applicability of these values to other homologous series being assumed, they have been used diagnostically to deduce the type of chain configuration present in the relevant liquids, and an attempt has been made to correlate any apparent changes in this configuration with differences in structure of the solids crystallising out at the freezing point.

Values of log *C* have been calculated from available viscosity data for hydrocarbons of the 2-methyl-, 1-phenyl-, 1-*cyclo*hexyl-, and 1-*cyclo*pentyl-alkane and Δ^1-*n*-alkene series; *n*-alkyl chlorides, bromides, and iodides; the methyl to *n*-octyl esters of the *n*-aliphatic acids; the ethyl alkyl and dialkyl ethers; methyl alkyl ketones; *n*-alkyl sulphides and *n*-alkanethiols; and *n*-alkyl cyanides. Plots (not reproduced) of these values against the length, *n*, of the alkyl chain, show that:

(1) In all the above series, the slope of the log *C*–*n* plot for the lower terms approximates closely to that of the corresponding plot for the *n*-alkane series up to $n = ca.$ 16, the inference being therefore that, as in the latter, the molecules in the liquids have the helical β-configuration.

(2) With the hydrocarbon series, the few points available for higher terms fall progressively below the extrapolation of the above lines, but the data are not sufficiently extensive or consistent to indicate conclusively either the precise points of inflexion or the slopes of the upper parts of the curves. In general, however, the latter are consistent with the assumption that they approximate to the slope of the *n*-alkane curve above C_{16}, and that the liquid molecules are therefore in the planar zig-zag α-form. Crystallographic confirmation of the existence of this α-form at the freezing point is only available for the

2-methylalkane series (Ställberg-Stenhagen and Stenhagen, *J. Biol. Chem.*, 1948, **173**, 383) but the observations by Krafft (*Ber.*, 1886, **19**, 2982) and Sherk, Augur, and Soffer (*J. Amer. Chem. Soc.*, 1945, **67**, 2239) on the dimorphism of hexadecyl-, octadecyl-, and eicosylbenzenes are relevant in this connection.

(3) With the ethyl esters, $C_nH_{2n+1}\cdot CO_2Et$, the log C–n plot shows a discontinuity at about $n = 13$ (myristate), the slope above this point being that characteristic in the alkane series of the planar zig-zag α-configuration. This agrees well with the recorded data on the freezing points and polymorphism of these esters, those below the myristate having been shown to crystallise when pure in the β-form, whereas above the myristate they tend to crystallise initially in the α-form, which is the stable form at the m. p. above ethyl pentadecanoate in the odd series, and above ethyl behenate in the even series (cf. Malkin, *loc. cit.*, 1931; Smith, *J.*, 1931, 802; 1933, 635; Mumford and Phillips, *Rec. Trav. chim.*, 1933, **52**, 175, 181; *J.*, 1934, 1657; Meyer and Reid, *J. Amer. Chem. Soc.*, 1933, **55**, 1574; van Bellinghen, *Bull. Soc. chim. Belg.*, 1938, **47**, 640).

No viscosity data appear to be available for the higher terms of the other series, and it is not therefore possible to check whether the log C–n plot exhibits a change of slope in the case of the higher halides, ketones, and nitriles, where the existence of α-forms has been demonstrated from crystallographic or freezing-point studies.

The validity of extending this method of approach to the *n*-aliphatic alcohols and acids is problematical in view of the circumstance that their log C values vary appreciably according to the temperature range involved, presumably owing to changing association. Elimination of this variable as far as possible by restricting consideration to values derived from measurements at 70—90° suggests, however, that in the alcohol series a change of slope of the log C–n plot occurs somewhere between C_8 and C_{16} [compare the finding by Malkin (*J. Amer. Chem. Soc.*, 1930, **52**, 3739) and by Wilson and Ott (*J. Chem. Phys.*, 1934, **2**, 231) that the alcohols from C_{12} upwards crystallise initially in the vertical α-form], whereas in the *n*-aliphatic acid series the log C values appear to be approximately linear with n from butyric to stearic, within the limits of experimental error, with a slope $\Delta\log C/\Delta n$ of *ca.* 0·081 [compare the crystallographic observation by Piper *et al.* (*J.*, 1926, 2310; *Trans. Faraday Soc.*, 1929, **25**, 348; *J. Amer. Chem. Soc.*, 1939, **61**, 577) that the fatty acids in this range exhibit a " tilted " long-spacing at their m. p.s].

Although, therefore, the correlation is incomplete, the evidence at present available appears to be generally consistent with the view that in non-associated aliphatic homologous series the intermolecular-force increment, as measured by the slope of the log C–n plot, and the form of the crystals to which the liquids initially set, are both determined by the chain configuration of the liquid molecules; the planar zig-zag α-configuration corresponding to $\Delta\log C/\Delta n = 0{\cdot}036$ and the α vertical-chain crystals observed in the longer-chain compounds of many series, and the helical β-configuration with $\Delta\log C/\Delta n = 0{\cdot}074$ and the β " tilted " chain crystals normal to the lower members of most aliphatic series.

Discussion.

From the arguments advanced in the first three sections of this paper it seems clear that the hexadecyl discontinuity in the physical properties of the liquid *n*-alkanes connotes a difference in molecular configuration which can be rationally explained by the hypothesis that above C_{16} the molecules in the liquid are in the planar zig-zag α-(*trans*-)form, whilst below C_{16} the chain configuration is that of an octagonal β-(approx. *cis*-)helix in which each C–C link of the zig-zag chain has been rotated through an angle of 56° to the *trans*-position. The survey summarised in the last section shows further that extension of similar ideas to other homologous series is consistent with the available viscosity and f. p. data.

The correlation which this hypothesis affords of the variation with chain length of the physical properties of liquid aliphatic homologues, their freezing points, polymorphism, and crystal structure, is *per se* strong presumptive evidence of its validity, but it carries with it certain important implications which must not be overlooked.

It implies in the first place that there is no free rotation about C–C links in the liquid molecules, the latter adopting an extended and more or less rigid linear chain structure which persists, despite thermal vibration, over a fairly wide temperature range.

It means, secondly, that there are two preferred rotational orientations about the C–C link, one (α) in which contiguous links are in the planar *trans*-position, the other (β) in which they approximate to the adjacent *cis*-position, with the second C–C link rotated through an angle of 56° to the *trans*-position. The factors determining this preference of position are obscure, but it would appear to involve some re-adjustment of orbitals, since the preference is passed on from atom to atom, the same positioning being followed by successive links throughout the molecular chain.

Thirdly, as an extension of the accepted dogma that the physical properties of a liquid depend on the configuration of its molecules, it implies that, in the case of the alkanes at least, the configuration adopted is closely bound up with, if not in fact determined by, spatial and intermolecular-force considerations, the stable form being that in which the molecule occupies the greater space and gives rise to the smaller intermolecular forces (cf. Fig. 5).

Fourthly, in conformity with modern ideas of liquid structure, it implies that in liquid aliphatic homologues the axially rotating cylindrical molecules, each in its van der Waals envelope of free space, are approximately parallel, and closely (hexagonally) packed.

Fifthly, it subscribes to the present day view that when a liquid crystallises without supercooling it does so in a crystal structure corresponding in molecular arrangement to that in the liquid; and as a corollary suggests that the tilt of the " tilted " chain crystals of the lower members of homologous series arises from uncoiling of the helical β-molecule.

Certain of these implications involve somewhat novel concepts which do not appear to be entirely in accord with current trends of thought, and until they have been submitted to more detailed theoretical and experimental examination it would be premature to consider any of the obvious and varied consequences of the basic hypothesis. On a practical point of detail, however, it is evident from the data reviewed above, that in considering molecular volume and intermolecular force functions in series of liquid aliphatic homologues, atomic and structural constants derived from the lower terms of a series must not necessarily be expected to apply additively to the higher members.

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