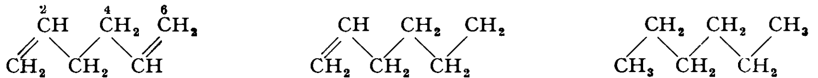
514. *The Configuration of Flexible C_6 Hydrocarbons in the Vapour Phase.*

By G. A. McD. Cummings, J. C. McCoubrey, and A. R. Ubbelohde.

New determinations of the viscosities of gaseous hydrocarbons in the range 20—200° are given for hexa-1 : 5-diene, 2 : 3-dimethylbut-2-ene, 2 : 3-dimethylbutane, 2 : 3-dimethylbuta-1 : 3-diene, and *cyclo*hexane. Comparisons of these with earlier results for *n*-hexane and hex-1-ene support the conclusion that in the temperature range studied the flexible molecules exhibit substantial "crumpling." Comparison between molecules of approximately the same molecular weight but with a range of flexibility wider than that of those previously studied shows that the average crumpling of the most flexible molecules probably increases somewhat as the temperature rises. Any such effect is, however, considerably smaller than would be required by existing theories of crumpling.

In a previous publication (McCoubrey, McCrea, and Ubbelohde, *J.*, 1951, 1961; see also *Discuss. Faraday Soc.*, 1951, **10**, 94) the average configurations in the vapour phase and their temperature dependence were compared for *n*- and *iso*-paraffins in the range C_5—C_8. From viscosity measurements, together with molecular volumes and entropies of vaporisation of the liquids at their boiling points, it was concluded that even in such short chains a substantial degree of crumpling occurs in the vapour phase and that any relative change of crumpling with temperature in the molecules studied was very small. Theoretically, the average degree of crumpling depends on the form of the repulsion barrier opposing free rotation about C–C bonds. At present, the mathematical form of this barrier is under discussion (Ubbelohde and Woodward, *Trans. Faraday Soc.*, 1952, **48**, 113). Even in the absence of definitive mathematical analysis it is possible to vary the barriers opposing rotation by synthesising the appropriate compounds. For example, from spectroscopic and thermodynamic data, the effect of unsaturation on the potential barrier restricting rotation about neighbouring C–C bonds and on the difference in the energy between the possible rotational isomers can be inferred (McCoubrey and Ubbelohde, *Quart. Reviews*, 1951, **5**, 364). A study of the following groups of hydrocarbons was undertaken to extend the range of flexibility investigated. To facilitate application of the kinetic theory of gases, all the hydrocarbons are based on a C_6 skeleton and have approximately the same molecular weight.

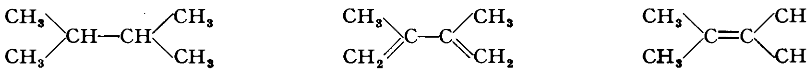
(a) *Hexa*-1 : 5-*diene, hex*-1-*ene,* n-*hexane.* Reduction in the number of hydrogen atoms in *n*-hexane by introduction of terminal isolated double bonds would be expected to lower the potential barrier opposing rotation of the rest of the molecules about the 2—3 and 4—5 C–C bonds and would thus facilitate crumpling.



Increased ease of crumpling.

←

(b) 2 : 3-*Dimethylbutane,* 2 : 3-*dimethylbuta*-1 : 3-*diene,* 2 : 3-*dimethylbut*-2-*ene.* It is known that introduction of unsaturation as above causes the potential barrier restricting rotation about the central C–C bond to be increased. The mono-olefin has no rotational isomers, and the central C–C bond of the diene has a bond order greater than unity as a result of conjugation. It would be expected that all the molecules in this group should be much less flexible than *n*-hexane.



Increased ease of rotation about the central C–C *bond.*

←

(c) cyclo*Hexane*. This molecule is likewise more rigid than *n*-hexane. It is assumed to be predominantly in the rigid "chair" form (Hazebroek and Oosterhoff, *Discuss. Faraday Soc.*, 1951, **10**, 87; Hassel, *Research*, 1951, **3**, 504). Results recorded in Tables 1 and 2 show that these expectations about the molecular configurations of the flexible molecules are in substantial agreement with the collision diameters based on viscosity measurements.

EXPERIMENTAL

Materials.—cyclo*Hexane*. This was prepared in this laboratory (Thompson and Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 349).

Hexa-1 : 5-*diene*. This was prepared by condensation of allyl chloride in presence of magnesium as described in *Org. Synth.*, **27**, 7).

A general treatment used for all the hydrocarbons involved purification by storage over sodium wire, refluxing, and finally distillation over sodium under dry oxygen-free nitrogen through a column packed with $\frac{1}{8}''$ glass helices. The distillate was then redistilled through a 6″ column packed with phosphor-bronze gauze (12 plates), with a reflux ratio of 20 : 1. A sample with boiling range 59·4—59·5°/758 mm. had n_D^{20} 1·4042 and ρ^{19} 0·692 ± 0·001 g./c.c.

2 : 3-*Dimethylbuta*-1 : 3-*diene*. Prepared by dehydration of pinacol with hydrobromic acid (*ibid.*, **1**, 448; **22**, 37), the product was washed several times with water (Farmer and Warren, *J.*, 1931, 3721) and dried over calcium chloride. After distillation, purification as above gave a sample boiling at 68·4—68·5°/760·9 mm. with n_D^{20} 1·4391 and ρ^{17} 0·729 ± 0·001 g./c.c.

2 : 3-*Dimethylbut*-2-*ene*. Methyl *iso*butyrate reacted with methylmagnesium bromide and hydrolysis then gave an alcohol which was dehydrated by distillation with iodine to a mixture of olefins (Howard, *J. Res. Nat. Bur. Stand.*, 1947, **38**, 365). Purified as above, it had boiling range 72·9—73·1°/757·5 mm., n_D^{20} 1·4122, $\rho^{12\cdot5}$ 0·716 ± 0·001 g./c.c.

2 : 3-*Dimethylbutane*. A crude specimen (Messrs. L. Light & Co.) was washed with, successively, concentrated sulphuric acid, sodium carbonate solution, and distilled water, and was dried ($CaCl_2$). After distillation, purification as above gave a fraction, b. p. 57·8—57·9°/760·8 mm., n_D^{20} 1·3750, n_D^{15} 1·3798, ρ^{12} 0·665 ± 0·001 g./c.c. The temperature coefficient of refractive index differs somewhat from previous data (Nat. Bur. Stand. Circular C 461, 1947, gives n_D^{20} 1·37495, n_D^{15} 1·37759). To test further for physical homogeneity and to obviate the risk of working with a constant-boiling mixture, the pressure was reduced to 10 cm. Hg and the selected fraction was refractionated. No difference was observed between the refractive indices of the first and the last portion separated in this way.

In working with the unsaturated compounds, it was important to verify that the properties measured did not refer to samples contaminated by polymerisation. Probably because of the precautions to avoid dissolved oxygen, no indication of polymerisation in the apparatus was observed. To check that no hydrocarbon polymer was deposited on the walls of the capillary the determinations at lower temperatures for the unsaturated compounds were repeated after the high-temperature determinations. The capillary was also recalibrated with dry air immediately after completion of the series with the hydrocarbon and no variation in r^4/L (cf. p. 2727) was observed.

Viscosities.—The apparatus and technique have been described (McCoubrey, McCrea, and Ubbelohde, *J.*, 1951, 1961). Measurements on the C_6 series of hydrocarbons are facilitated by their convenient vapour pressures. Compared with the earlier work quoted, some reduction in probable error of measurement has been achieved. The coefficient of viscosity was calculated as previously detailed, the usual correction for slip being made. No allowance was included for any dependence on pressure of η. No correction was made for departure from ideal-gas laws, since second virial coefficients are not available for all the selected compounds. Although this was was not explicitly stated in the previous publication, the use of a liquid-air trap in the capillary effusion apparatus introduces the possibility of Knudsen flow at the low-pressure end of the capillary. However, calculation shows that under the conditions used, the contribution to the total resistance to flow from the Knudsen region is less than 0·1%. This was neglected.

DISCUSSION

To facilitate rapid comparison between molecules, lines of closest fit for log η–log T were calculated (see Table 3). Interpolated viscosities at given temperatures were obtained as in Table 1. An estimate of the accuracy of measurement may be obtained from the mean deviation from lines of closest fit (Table 3).

The values of the viscosities for the C_6 series are given in Table 1. Table 2 gives the ratios R at different temperatures of the viscosities relative to the stiffest molecule 2 : 3-dimethylbut-2-ene. Table 2 also gives the temperature trend of these ratios by comparison of $(R_{450} - R_{300})/R_{300}$.

TABLE 1. *Viscosities (in poises* × 10^7*) of* C_6 *hydrocarbons interpolated from* log η–log T *lines of closest fit.*

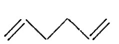
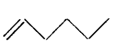
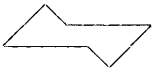
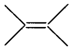
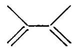
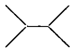
Temp., ° K							
300	717·1	676·2	637·1	699·7	739·4	727·1	719·5
350	837·2	785·1	742·8	805·2	831·6	835·6	829·3
375	897·4	839·5	795·8	857·4	876·8	889·2	883·9
400	957·4	893·9	848·7	909·5	920·9	942·5	938·4
425	1018	948·2	901·7	961·2	964·5	995·4	992·4
450	1078	1003	954·7	1013	1007	1048	1046

TABLE 2. *Ratios* (R) *of viscosities of* C_6 *hydrocarbons at different temperatures (relative to* 2 : 3-*dimethylbut*-2-*ene).*

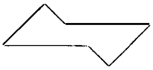
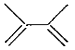
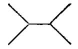
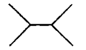
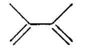
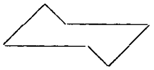
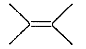
Temp., ° K						
300	0·972	0·915	0·861	0·946	0·983	0·973
350	1·007	0·944	0·893	0·968	1·005	0·997
375	1·023	0·957	0·908	0·978	1·014	1·008
400	1·039	0·971	0·922	0·988	1·023	1·019
425	1·055	0·983	0·935	0·997	1·032	1·029
450	1·071	0·996	0·948	1·006	1·041	1·039
R_T = Ratio at temperature T ° (K) $\dfrac{(R_{450} - R_{300})}{R_{300}}$	0·102	0·089	0·101	0·063	0·059	0·068

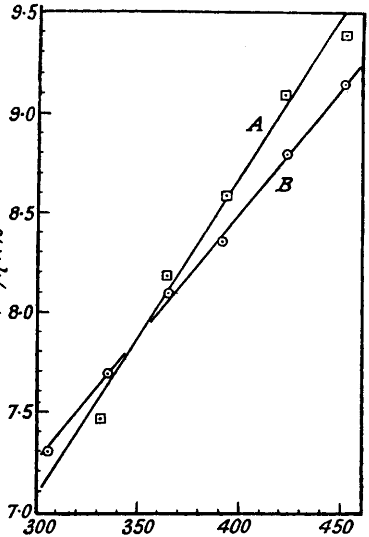
TABLE 3.

Carbon skeleton	Line of closest fit log $\eta = s \log T + C$			Simple kinetic-theory collision parameter $\mathscr{A} = \sqrt{MT}/\eta \times$ const.		Sutherland constant	Sutherland collision area
	s	C	mean $\Delta = \lvert C - (y - sx) \rvert$	Temp = 300° K	Temp. = 450° K	S	(10^{-16} cm.^{2})
	1·005	6·633	0·003	0·219	0·178	509	17·3
	0·9721	6·578	0·003	0·235	0·194	392	23·8
	0·9976	6·667	0·002	0·252	0·206	384	25·6
	0·9244	6·433	0·001	0·223	0·188	282	24·2
	0·9022	6·373	0·002	0·216	0·183	256	24·5
	0·9128	6·416	0·003	0·227	0·192	276	25·0
	0·7638	6·023	0·003	0·215	0·193	168	29·2

Tables 1 and 2 show two significant features in this group of C_6 hydrocarbons. First, the viscosity of *n*-hexane at any temperature in the range covered is smaller than that of any of the other compounds. This implies that the (uncorrected) kinetic-theory collision areas of all the other hydrocarbons are smaller than that of *n*-hexane (cf. $\mathscr{A}$ in Table 3). However, the ratios in Table 2 show that differences in apparent collision area are quite small. This means that the more flexible molecules do not behave as if they were fully extended in the vapour at ordinary temperatures. Secondly, the ratios R all show a definite trend with temperature, which exceeds possible experimental error. If we use the function $(R_{450} - R_{300})/R_{300}$ as a measure of this trend, the function is found to have its largest value for the most flexible molecule hexa-1 : 5-diene and its lowest value for the much less flexible 2 : 3-dimethylbuta-1 : 3-diene. It is also interesting to compare the values of this function for *n*-hexane with the variation in the relative average square length (L^2) and square radius (r^2) of the *n*-paraffin hydrocarbons deduced theoretically by Taylor (*J. Chem. Phys.*, 1948, **16**, 259) for long-chain compounds, which is of the order of 20% for the temperature range 300—450° K. So far as these values are comparable, the theoretical trend $(R_{450} - R_{300})/R_{300} = (<r^2>_{450} - <r^2>_{300})<r^2>_{450}$ would be 0·25 if it is assumed that $<r^2>$ for the stiffest reference molecule does not change with temperature.

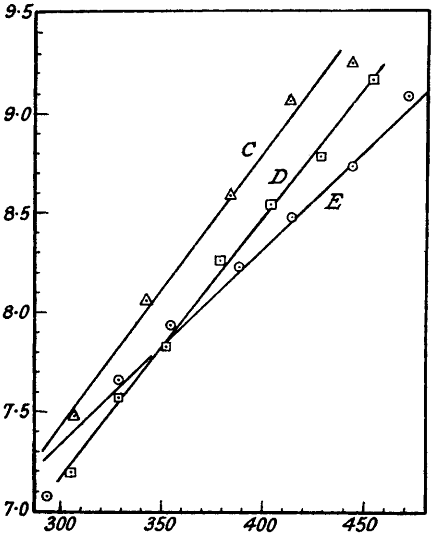
It seems clear that even for the most flexible molecules the increase in crumpling with temperature, as calculated from viscosity collision diameters, is much less than could be attributed to the fact that Taylor's calculation does not apply accurately to such short chains, or to the fact that viscosity collision diameters are not immediately comparable with $<r^2>$ values as calculated by Taylor. In the present state of our knowledge a preferable explanation of the low temperature coefficient associated with viscosity collision diameters is that the potential barrier opposing crumpling of the molecule is less extensive than was postulated by Taylor. Possible forms of potential barrier which would agree better with the present findings have been discussed by Ubbelohde and Woodward (*loc. cit.*).

FIG. 1. *Sutherland plots.*



A, 2 : 3-*Dimethylbut*-2-*ene.*
B, 2 : 3-*Dimethylbutane.*

FIG. 2. *Sutherland plots.*



C, cyclo*Hexane.*
D, 2 : 3-*Dimethylbuta*-1 : 3-*diene.*
E, *Hexa*-1 : 5-*diene.*

The possibility that the average configuration of a flexible molecule changes with temperature provides a new contribution to the temperature coefficient of the viscosity of the vapour. In cases where this contribution is important, the Sutherland or the Hirschfelder interpretation of temperature coefficient will be inadequate. To examine this new concept Sutherland and Hirschfelder parameters are first calculated with neglect of any contribution to the temperature coefficient arising out of molecular flexibility. Sutherland constants and collision areas calculated from graphical plots of $T^{3/2}/\eta$ against T are given in Table 3. The accuracy with which the Sutherland relationship applies is illustrated in the Figures. As found previously (McCoubrey, McCrea, and Ubbelohde, *loc. cit.*) the experimental values of viscosity fit more closely to a logarithmic relation $\log \eta = s \log T + C$.* Values of s and C and probable errors are recorded in Table 3.

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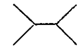
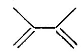
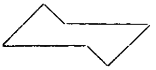
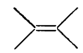
* This conclusion extends the findings of Chapman and Cowling ("The Mathematical Theory of Non-Uniform Gases," Cambridge Univ. Press, 1939, pp. 223, 229) to more complex molecules. The fact that in Table 3 the smallest values of s are found for the stiffest molecules is formally in agreement with the results for simpler molecules (*op. cit.*, p. 223). An important difference is that some of the C_6 molecules can yield under impact, by means of quite extensive relative movements of the atoms within the molecule. No mathematical analysis is yet available for determination of the conditions of collision for which such internal relative movement of the atoms can become important. The problem is of considerable interest for the study of the reactivity of hydrocarbons in relation to structure (cf. Ubbelohde, *Rev. Inst. franç. du Pétrole et Ann. Combust. Liquid,* 1949, **4**, 488; Ubbelohde and McCoubrey, *Discuss. Faraday Soc.*, *loc. cit.*).

The Hirschfelder constants given in the last two columns of Table 4 were deduced from Sutherland's constant and slopes of lines of closest fit by using the tables relating $\boldsymbol{k}T/\varepsilon$, S/T, and s as given by Hirschfelder (*Trans. Amer. Soc. Mech. Eng.*, 1949, **71**, 921). r_0 is deduced from the equation $\eta \times 10^7 = 266{\cdot}93(MT)^{\frac{1}{2}}[r_0]^{-2}(V)/W^2(2)$, the tables relating V and $W^2(2)$ with $\boldsymbol{k}T/\varepsilon$ being used.

The parameters uncorrected for molecular flexibility deduced for Sutherland and Hirschfelder's different molecular models from viscosity data show the same general trends. Hexa-1 : 5-diene has the largest force parameter and the smallest collision diameter, and 2 : 3-dimethylbut-2-ene has the lowest force parameter and the largest collision diameter. However, these force parameters S and $\varepsilon/\boldsymbol{k}$ cannot be taken as measures of the force field of a molecule since they are extremely sensitive to slight changes in the temperature dependence of viscosity. If the geometry of a molecule is temperature-dependent, as we should expect for flexible molecules with low barriers to rotation about C–C bonds, the uncorrected value of $\varepsilon/\boldsymbol{k}$ deduced from viscosity would depend on the temperature variation of average molecular configuration. A measure of the force field of the molecule less dependent on such geometrical effects may be calculated from other data on the molecules.

TABLE 4.*

Carbon skeleton	$\varepsilon/\boldsymbol{k}$, from b. p. data (° K)	$\varepsilon/\boldsymbol{k}$, from second virial data (° K)	From viscosity temp. coeff. $\varepsilon/\boldsymbol{k}$ (° K) (uncorr. for flexibility)	r_0 (cm.$^{-8}$)
	463	—	508	5·30
	468	—	356	6·01
	475	213 [a]	370	6·18
	460	217 [b]	256	6·39
	475	—	235	6·40
	492	212 [a]	256	6·46
	482	—	153	7·09

[a] Lambert *et al.*, *Proc. Roy. Soc.*, 1949, **176**, *A*, 113. Waddington *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 3905.

* Results in Table V given by McCoubrey, McCrea, and Ubbelohde (*loc. cit.*, p. 1970) should be multiplied by 1·23 to bring them into line with the method of calculation described in this paper, which is based on first calculating Sutherland's constant.

In Table 4, column 2 gives values of $\varepsilon/\boldsymbol{k}$ from boiling-point data. These are deduced by using the relation $\varepsilon/\boldsymbol{k} = 1{\cdot}39T_b$ (cf. Hirschfelder, *loc. cit.*) where T_b is the boiling point in degrees absolute. Although the numerical factor may not be appropriate for these molecules, the data show that $\varepsilon/\boldsymbol{k}$ is in fact not sensitive to the arrangement of bonds. Column 3 gives parameters $\varepsilon/\boldsymbol{k}$ calculated by a trial-and-error method by using the expression (1) for the second virial coefficient of the vapours.

Results for a series of butenes (Roper, *J. Phys. Chem.*, 1940, **44**, 835) indicate that the second virial coefficient $B(T)$ is not greatly affected by molecular shape or by the introduction of an olefinic double bond (cf. also Hirschfelder, *J. Chem. Physics*, 1942, **10**, 207). Equation (1) relating this coefficient to $\varepsilon/\boldsymbol{k}$, *viz.*,

$$B(T) = \tfrac{2}{3}\pi N r_0{}^3 \mathrm{F}(\varepsilon/\boldsymbol{k}T) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

shows that $\varepsilon/\boldsymbol{k}$ is relatively insensitive to small changes in the second virial coefficient. On this basis, " true " force parameters $\varepsilon/\boldsymbol{k}$ should vary but little for the series of C_6 hydrocarbons studied.*

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* A possible exception to the statement that the attractive force field between molecules should not be sensitive to the presence of double bonds or to exact molecular shape may arise in 2 : 3-dimethylbuta-1 : 3-diene, where the conjugation might substantially modify the ionisation energy I. This may be illustrated by reference to the approximate expression for the energy of intermolecular attraction due to dispersion forces $E = -3I\alpha^2/r_0{}^6$ due to London (*Z. physikal. Chem.*, 1930, **11**, *B*, 222).

The penultimate column of Table 4 shows that $\varepsilon/\boldsymbol{k}$ calculated from viscosity is very far from being independent of molecular shape. In fact, the values show the definite trend to be larger for the more flexible molecules. We attribute this to modification of the temperature coefficient of viscosity by change in average configuration with temperature. Calculations of Sutherland or Hirschfelder constants which do not allow for this factor lead to incorrect force parameters.

A third argument in support of the conclusion that the temperature trend in viscosity of the more flexible molecules includes a considerable contribution from the change in average molecular configuration with temperature is derived from more detailed consideration of the ratio of viscosities of pairs of molecules. If the Sutherland expression $= AT(1 + S_0/T)$ applies where S_0 is the true force field parameter, the temperature effects due to changes of configuration being neglected, then for a pair of molecules

$$\frac{\eta_1}{\eta_2} = \frac{A_1}{(S_{01} + T)} \cdot \frac{(S_{02} + T)}{A_2} = R$$

The true S_0 parameters are closely related to the true values of $\varepsilon/\boldsymbol{k}$ and should not differ by more than a few per cent for hydrocarbons of the same number of carbon atoms. A difference between η_1 and η_2 of this order would involve a temperature trend $(R_{450} - R_{300})/R_{300}$ of $\ngtr 1\%$. The much larger trend of the ratio recorded in Table 2 is attributed to the variation in average molecular configuration with temperature.

The conclusion from the studies in this and preceding papers is that in molecules where crumpling can occur the average degree of crumpling in the vapour phase is appreciable even at ordinary temperatures. Some further increase in crumpling occurs as the temperature rises.

Further experiments are in hand to test this conclusion with longer carbon skeletons and with other molecular shapes.

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