Journal of Fluorine Chemistry, 50 (1990) 89–99

Received: February 23, 1990; accepted: April 30, 1990

BOILING POINT RELATIONS IN THE HALOGENATED ETHANE SERIES

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SUMMARY

Patterns of boiling points among the fifty five halogenated ethanes are illustrated. The relative boiling points of the forty-six isomers in the system are summarized in terms of three rules depending simply on halogen distributions. The unknown boiling points of CH_2FCCl_3 and CH_2FCHCl_2 are estimated as 74.4±1°C and 88.8±1°C respectively from the patterns and rules. Variations in boiling points are rationalized mainly in terms of intermolecular repulsions between dipoles of the same kind, and attractions between dipoles of opposite polarity.

INTRODUCTION

There are 55 halogenated ethanes, ($C_2Cl_xF_yH_z$) of which 46 are positional isomers. The known boiling points are collected in Figure 1 where the x, y coordinates are specified and z is given by (6-x-y). The boiling points of CH_2FCCl_3 and CH_2FCHCl_2 have not been reported. A choice had to be made between quoted values for some compounds albeit guided by the patterns discussed later. The right angled presentation is easier to comprehend than the more usual ternary triangular one for this particular series. The boiling points are of interest because various thermodynamic properties can be calculated from them. For example the suitability of compounds as CFC substitutes for refrigerants can be assessed [1]. Also the pattern of ethane derivatives should be helpful in elucidating the pattern among the 336 substituted propanes.

0022-1139/90/$3.50

RESULTS

The most widely applied relation between boiling points in series was devised by Kinney [2]. It was based on the old Walker relation b.pt./K = pM^q where M is the relative molecular mass (RMM) and p and q are constants with the latter close to a third for many homologous series. Kinney linearized the boiling points of the C_nH_{2n+2} series by replacing M with appropriate contributions, a for carbons and b for hydrogens, which he named boiling points numbers (BPN). A linear plot of b.pt/°C against $[n\ a + (2n+2)b]^{1/3}$, including the value at n = 0, was obtained by a suitable choice of a and b values. The equation to the line was $\text{b.pt}/^{\circ}\text{C} = 230.14\ (\Sigma\text{BPN})^{1/3} - 543$.

The BPN of a substituent in a hydrocarbon derivative could then be found by calculating the BPN of the compound from its boiling point via the equation and subtracting the C and H contributions. This approach had to be modified by Anderson [3] for the n-chlorofluoroalkanes where group contributions rather than atom ones were required. Ten constants for substituted methyl groups, and six for substituted methylenes, were derived. Even so predictions were restricted to the central compounds in Figure 1 containing at least one each of H, Cl and F in order to limit errors. Thirteen constants in all were used to predict boiling points of 25 substituted ethanes with an average error of $\pm 5.2^{\circ}$C ranging from 0.8 to 14.9°C.

In spite of these errors the plot of BPN against RMM (Figure 2) does reveal some interesting features. Firstly, certain group combinations produce isomers of nearly equal boiling points. This holds for combinations across diagonals of the three parallelograms e.g. $CClF_2CHF_2 \equiv CHClFCF_3$ or across adjacent ones e.g. $CHClFCHClF \equiv CCl_2FCH_2F$ and for edge combinations eg $CHClFCHClF \equiv CHCl_2CHF_2$. Secondly the negative slopes show an anomalous increase in BPN with RMM when F is replaced by H, and thirdly the methyl contribution seems unique in that it dips 2.2 units below the pattern as indicated by the dotted lines in Fig. 2.

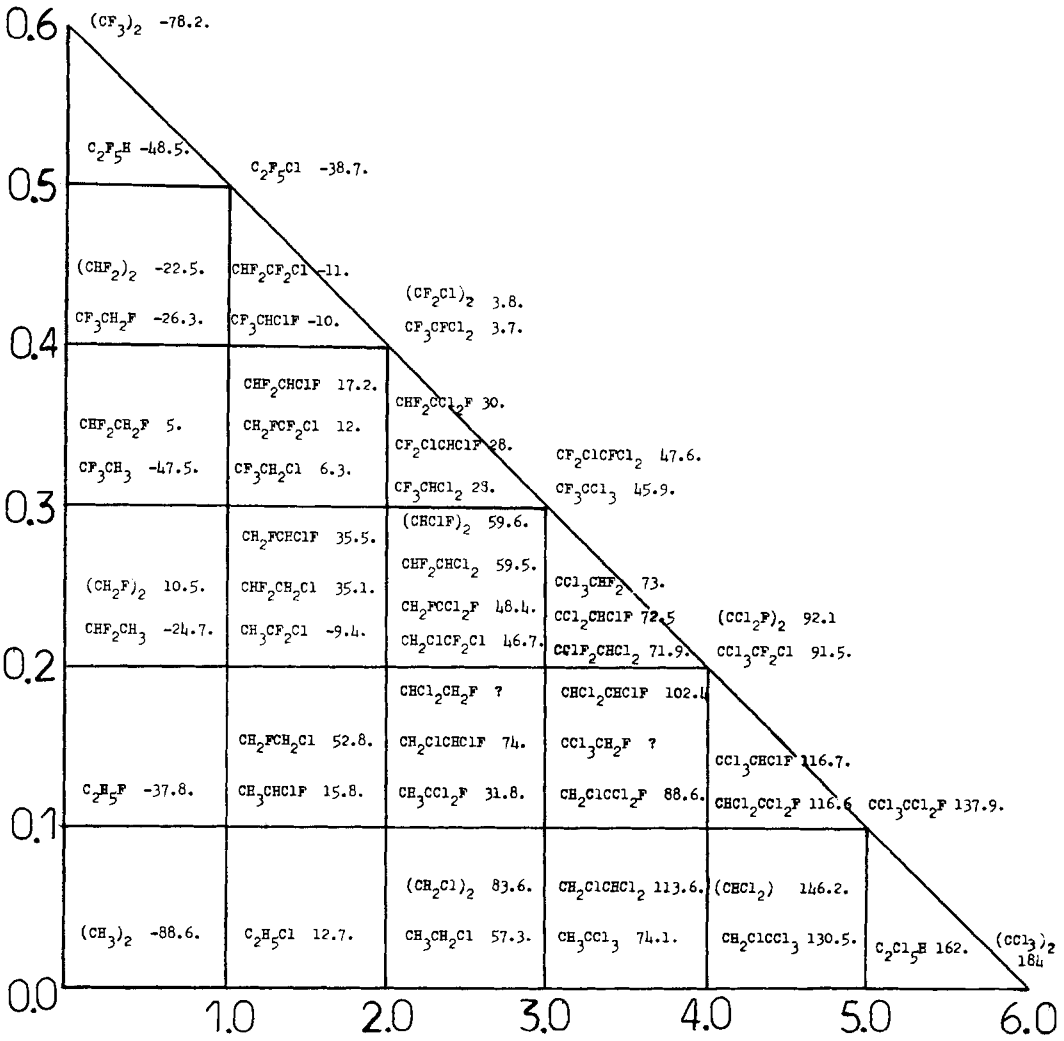

Fig. 1. Boiling points of the halogenated ethanes $C_2H_xF_yH_{(6-x-y)}$.

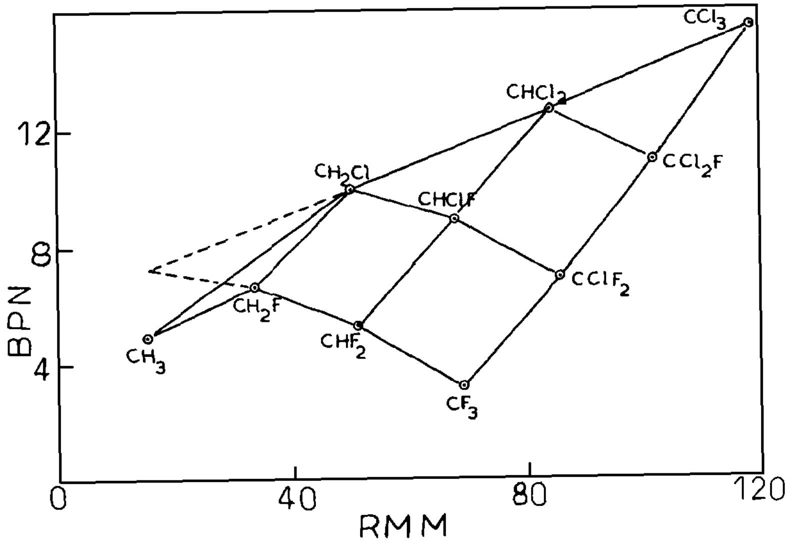

Fig. 2. The dependence of group boiling point numbers (BPN) on molecular weight (RMM).

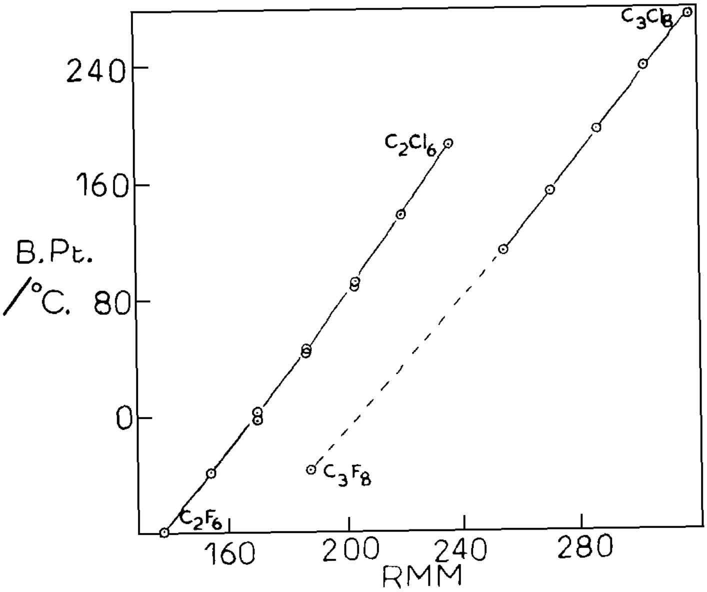

Fig. 3. The dependence of boiling points in the halogenated ethane and propane series on molecular weight.

The peripheral boiling points, ignored by Anderson for compounds with one element absent, form three distinct series. Only the C_2F_6 - C_2Cl_6 series has an approximately linear increase of boiling points with RMM or degree of chlorination. More exactly there are two linear relations if average values of isomer boiling points are taken. Above half substitution b.pt./^{o}C = -476.3 + 2.79 RMM (r = 0.9999)
and below b.pt./^{o}C = -429.6 + 2.54 RMM (r = 0.9999). Similar linear relations hold for halogenated methanes and propanes (Figure 3). Along the horizontal C_2H_6 - C_2Cl_6 series the isomers no longer have equal boiling points and the boiling point relations are distinctly non-linear. Linear relations can be obtained however using the Δ = A-BR equation introduced previously [4] where Δ is the increase in boiling point of the chlorinated derivative over ethane, and R the mass ratio of ethane to its derivative. A delta-wing shaped curve is produced dihedrally bent across the half substitution level where the chord is at a maximum (Fig. 4).

The least regular series is from C_2H_6 - C_2F_6 where there are minima at both ends. Again the maximum difference between isomers occurs at half substitution (Figure 5). In view of these three different types of variation it is not surprising that the pattern of boiling points as a whole is irregular and indifferently fitted by the Kinney treatment. Nevertheless if only the difference in isomer boiling points is considered then some simple rules emerge.

1. Isomers with the same number of halogens on both carbons boil at approximately the same temperature.
2. Isomers with different numbers of halogens on each carbon boil at different temperatures. The difference varies with the number of hydrogens in the order 3H>4H>2H and in the approximate ratio 4/3/1.
3. The lower boiling isomers have the less symmetrical halogen distribution.

It is interesting to note in connection with rule 1, that Cl and F produce equal F^{19} nmr shifts when α-substituted into ethyl fluoride [5].

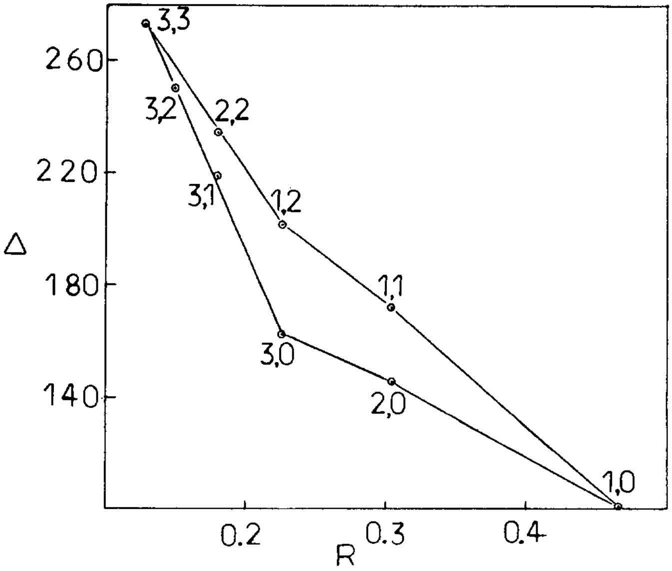

Fig. 4. The relation of boiling point elevations (Δ) of hydrochloroethanes over ethane to the mass ratio (R) of ethane to chlorinated derivative. (The numbering refers to the chlorines on each carbon).

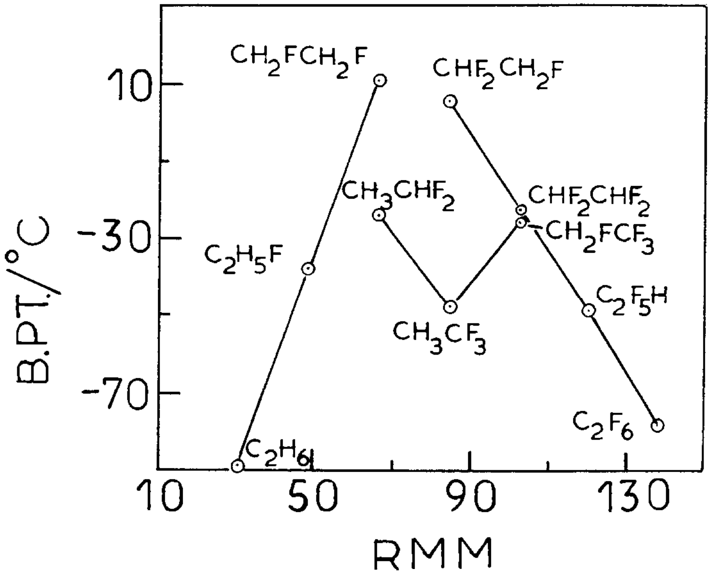

Fig. 5. The dependence of boiling points in the hydrofluoroethane series on molecular weight.

The unknown boiling points of CHF_2CCl_3 and CHF_2CHCl_2 can now be estimated from some of the aforementioned relations and rules. The approximate linear relation for the C_2F_6 - C_2Cl_6 series holds for series with constant hydrogen content along lines parallel to the hypotenuse (see Fig. 1).

For example the mean difference between the five pairs of compounds with zero and two hydrogens (i.e. vertically displaced in Figure 1) is $54.8 \pm 0.3^{\circ}C$. The mean differences (δ) between successive pairs changes slowly as shown with increasing chlorination.

$$\begin{tikzcd}
 & \mathrm{CF_3CH_2Cl} \arrow[r] & \mathrm{CF_2ClCH_2Cl} \arrow[r] & \mathrm{CFCl_2CH_2Cl} \arrow[dr] & \\
\mathrm{CF_3CH_2F} \arrow[ur] \arrow[dr] & & & & \mathrm{CCl_3CH_2Cl} \\
 & \mathrm{CF_2ClCH_2F} \arrow[r] & \mathrm{CCl_2FCH_2F} \arrow[r] & \mathrm{CCl_3CH_2F(?)} \arrow[ur] & \\
\delta/^{\circ}C \;=\; & 36 & 38 & 41 & 42
\end{tikzcd}$$

where the boiling point of CCl_3CH_2F is between 89.4 and 88.5°C by forward and backward interpolation respectively.

Similarly the boiling point of $CHCl_2CH_2F$ interpolates between 74.5 and 73.6°C from the series

$$\begin{tikzcd}
 & \mathrm{CHF_2CH_2Cl} \arrow[r] & \mathrm{CHFClCH_2Cl} \arrow[dr] & \\
\mathrm{CHF_2CH_2F} \arrow[ur] \arrow[dr] & & & \mathrm{CHCl_2CH_2Cl} \\
 & \mathrm{CHClFCH_2F} \arrow[r] & \mathrm{CHCl_2CH_2F(?)} \arrow[ur] & \\
\delta/^{\circ}C \;=\; & 30 & 39 & 40
\end{tikzcd}$$

(The low first difference may indicate that the quoted boiling point of 5°C for CH_2FCH_2F is too high. A boiling point of -4° to -5°C would give a more consistent set of δ values).

These estimates of boiling points are consistent with rule 1 since the corresponding isomers with equal numbers of halogens on both carbons boil at the same temperatures within the error limits : viz, quoted values for CH_2ClCCl_2F are 88.4 and 88.8°C and for $CH_2ClCHClF$ 73.9 and 76°C.

A third estimate of the unknown boiling points uses the Δ = A-BR relation in a way which relates boiling points of methane and ethane derivatives. Thus insertions of CCl_2 into chloromethanes produce ten ethanes containing the CCl_3 group. The Δ v R plot is shown in Fig. 5 and the data in Table 1.

TABLE 1

Elevation of boiling points caused by CCl_2 insertion in C-Cl bonds of chloromethanes

Compound (1)	B.pt 2	Compound (3)	B.pt. 4	R $\frac{RMM(3)}{RMM(1)}$	Δ 2-4
CH_3CCl_3	74.0	CH_3Cl	-24.1	0.378	98.1
CH_2FCCl_3	?	CH_2FCl	-9.0	0.452	?
CH_2ClCCl_3	130.5	CH_2Cl_2	39.8	0.506	98.2
CHF_2CCl_3	73.0	$CH F_2Cl$	-40.7	0.510	113.7
$CHClFCCl_3$	116.7	$CHCl_2F$	8.9	0.554	107.8
CF_3CCl_3	45.9	CF_3Cl	-81.4	0.558	127.3
$CHCl_2CCl_3$	162	$CHCl_3$	61.2	0.590	100.8
CF_2ClCCl_3	91	CF_2Cl_2	-29.8	0.593	120.8
CCl_2FCCl_3	137.9	CCl_3F	23.8	0.624	114.1
CCl_3CCl_3	184.6	CCl_4	76.7	0.650	107.9

It can be seen that Fig. 5 is a reorientated version of Fig. 2 in which BPN s were plotted against RMM. Hence the point corresponding to CH_3CCl_3 is again treated as exceptional and excluded from any smooth interpolations. The elevation expected for CH_2FCCl_3 is obtained instead by two parallel linear extrapolations and one slightly curved one. The weighted mean boiling point of CH_2FCCl_3 is then 89.7 ± 1°C. A similar method for estimating the boiling point of $CH_2F\ CHCl_2$ uses the insertion reaction $\div C{-}F \xrightarrow{CH_2} \div C{-}CH_2F$. These estimates together with those from Anderson's BPN's are collected in Table 2.

TABLE 2

Estimation of unknown boiling points/°C

Compounds		Method of estimation
CH_2FCHCl_2	CH_2FCCl_3	
74±1	89±1	By series differences at constant hydrogen.
75±1	88.6±0.2	By isomer comparison
74±1.5	89.7±1	By Δ = A-BR relations
73.2 ± 3.5*	101.7 ± 8.6*	By Anderson's BPN's [3]

*These errors are the mean (calc.-found) values for ethanes containing 2 and 3 chlorines respectively.

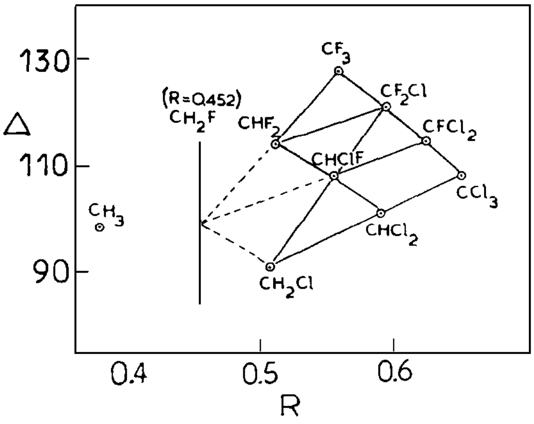

Fig. 6. Differences between vaporization heats of isomers relative to the lower value for series with the same number of hydrogen atoms. (The figures are x, y coordinates for locating the isomer positions in Fig. 1).

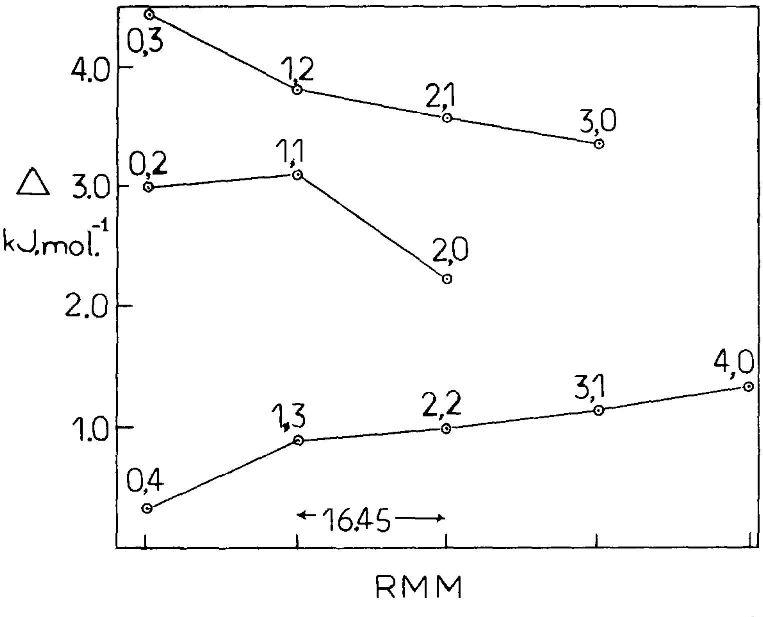

Fig. 7. The relation of boiling point elevations (Δ) of trichloromethyl substituted ethanes over ethane to the mass ratio of ethane to substituted ethane. (Only the groups attached to CCl_3 are shown).

DISCUSSION

The pattern of boiling points can be rationalised most simply in terms of dipolar forces. The helical nature of PTFE, and according to recent calculations [6] of fluorocarbons as small as C_4F_{10}, can be ascribed to intramolecular repulsions among the $\overset{+\!\!\longrightarrow}{C - F}$ dipoles which relieve strain. Hence it is feasible to postulate similar intermolecular repulsions, reaching a maximum for CF_3 groups, which reduce intermolecular attractions and lower boiling points. For hydrocarbons, with reversed polarity in $\overset{\longleftarrow\!\!+}{C - H}$ dipoles, repulsions are again maximized for methyl groups but less strongly than for CF_3 groups (See BPN contributions in Fig. 2). If hydrogen is present in the halogenated ethanes repulsions are counteracted by dipole attractions between dipoles of opposite polarity viz $\overset{+\!\!\longrightarrow}{C - F}$ $\overset{+\!\!\longrightarrow}{H - C}$ and this effect is at a maximum with single C - H dipoles.

These postulates are best illustrated by comparing isomer differences. One can convert boiling point differences between isomers to energy differences by using Trouton's rule assuming a constant vaporization entropy of 85 $JK^{-1}mol^{-1}$. The energy differences, at locations (x,y) in Figure 1, are plotted in Fig. 7 for series with the same numbers of hydrogens. These series run parallel to the hypotenuse in Fig. 1.

The half substituted isomers exhibit the largest difference because each lower boiling isomer combines the most repulsive CH_3 and CX_3 groups. The next largest differences occur above half hydrogen substitution when four hydrogens are present. In this series the lower boiling isomers have methyl groups and single hydrogens on the other carbon atom which leads to dipole attractions reducing the overall repulsions. The isomers in the (2,0) position show a smaller difference because the smaller carbon-chlorine dipole is less strongly attracted by H - C than is the C - F dipole.

Finally the series with two hydrogens present show the smallest differences. The lower boiling isomers contain both hydrogens on one carbon leaving CX_3 groups with high repulsions. However this is effectively counteracted in the higher isomers with <u>pairs</u> of $\overset{\longleftarrow\!\!+}{C - H}$ dipoles attracted to $\overset{+\!\!\longrightarrow}{C - X}$ dipoles opposed by <u>pairs</u> of CX_2 repulsions. The interactions increase with fluorine content and hence the decreasing differences from positions (4,0) to (0,4).

The approximately linear increase in boiling point along the C_2F_6 - C_2Cl_6 series indicates that polarizability variation is the predominant influence but even in this series dipole effects are noticeable. An inflection occurs at half substitution and there is a slight difference in isomer boiling points with the less symmetrically substituted isomers having the lower boiling points. In the C_2H_6 - C_2Cl_6 series the linear Δ = A-BR is indicative of polar influences. In all series inflections or turning points occur at half substitution associated with maximum repulsions of CH_3 or CX_3 groups.

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