

CHROM. 11,771

ANOMALIES IN THE GAS CHROMATOGRAPHIC BEHAVIOUR OF SUBSTANCES FACILITATING A RING CONFORMATION THROUGH THEIR PROPYL GROUP

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(Received February 6th, 1979)

SUMMARY

The applicability of precise gas chromatographic measurements has been demonstrated for the identification of very fine structural features of compounds. On the basis of the gas chromatographic behaviour of five classes of unsaturated hydrocarbons and four classes of compounds containing hetero-atoms, it is concluded that retention anomalies are to be expected for compounds with molecular structures that make it possible to form a ring conformation of the propyl group with the π -electron system of the remainder of the molecule and that this phenomenon is a common feature of the compounds with such structures.

INTRODUCTION

During the investigation of the relationship between the structures and gas chromatographic behaviour of linear alkenes on squalane stationary phase^{1,2}, an anomalous behaviour was found for 1-pentene, *trans*-2-hexene, *trans*-3-heptene, *trans*-4-octene and other *trans*-4-alkenes; the anomalies were systematic and always took the form of lower retention indices. The occurrence and the values of these anomalies suggested a particular steric arrangement of these compounds. Such considerations led us to the formulation of a hypothesis about the possibility of forming a suitable ring conformation that permits intramolecular orbital interactions².

Similar anomalies have also been found for structures with acetylene linkages³ and with the π -electron cloud of the aromatic nucleus^{4,5}. Our measurements were confirmed by a number of other workers dealing with *n*-alkenes⁶⁻⁹, *n*-alkynes¹⁰ and alkylbenzenes^{11,12} and they also evoked the interpretation of this phenomenon by means of quantum chemistry^{13,14} and NMR spectroscopy¹⁵.

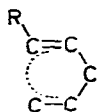
On the basis of the evaluation of recent literature data and our further measurements, we have tried to demonstrate the general character of the mentioned con-

formational type and to establish that precise gas chromatographic measurements are useful in the investigation of very fine conformational deviations.

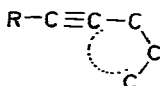
THEORETICAL

Gas chromatography offers the advantage of measuring the retention of volatile compounds in a state near to infinite dilution during the gas chromatographic separation. Intermolecular interactions found with these compounds in the liquid or solid state are substantially suppressed and even fine intramolecular structural interactions are then reflected in the retention indices.

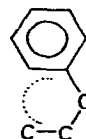
Anomalies appear in the retention behaviour of *n*-alkenes, *n*-alkynes and alkylbenzenes for compounds with the following structural arrangements:



1-pentene, *trans*-2-hexene, *trans*-3-heptene, *trans*-4-octene and higher *trans*-4-alkenes

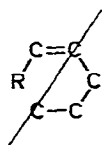


1-pentyne, 2-hexyne, 3-heptyne, 4-octyne and higher 4-alkynes

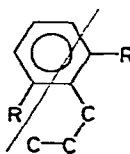
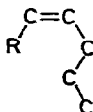


n-propylbenzene, most alkyl derivatives of *n*-propylbenzene

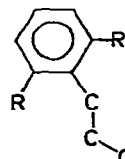
In contrast, such arrangement must be suppressed as a consequence of steric hindrance with the *cis*-form of *n*-alkenes and *o*-dialkyl derivatives of *n*-propylbenzene:



cis-2-hexene, *cis*-3-heptene, *cis*-4-octene and higher *cis*-4-alkenes



1,3-dimethyl-2-propylbenzene and other 1,3-dialkyl-2-propylbenzenes



EXPERIMENTAL

Retention data published in our previous papers^{2,5,16-18}, new measurements of retention indices^{19,20} and literature data^{8-12,21-23}, as listed in Table I, were used in this study.

The anomalous behaviour of various substances in their respective homologous series is derived from the dependence of increments, I_{CH_2} , or H , on the number of carbon atoms and from the dependence of retention index differences of the neighbouring positional isomers, δI , on the double-bond position, as well as from the corresponding dependences of the boiling points on the number of carbon atoms in the molecule of the respective derivative.

TABLE I
SURVEY OF THE DATA UTILIZED

Type of compound	Range	Stationary phase	Reference
<i>n</i> -Alkenes	C ₅ -C ₁₆	Squalane	2, 16
	C ₄ -C ₆	Squalane	21, 22
	C ₁₅ -C ₁₈	Apiezon L, Carbowax 20M	20
<i>n</i> -Alkynes	C ₃ -C ₇	Squalane	22
	C ₆ -C ₁₄	Squalane, Apiezon L, polyphenyl ether, polyethylene glycol 4000	10
		Squalane	20
<i>n</i> -Alkadienes	C ₄ -C ₈		
Cycloalkenes	C ₆ -C ₁₂		
	cyclopentenes	Squalane	
	C ₇ -C ₁₃		
Alkylbenzenes	cyclohexenes	Squalane	9
	C ₇ -C ₁₆	Squalane, acetyl tributyl citrate, triscyano- ethoxypropane	5, 17
	C ₆ -C ₁₄	Squalane	12
<i>n</i> -Carboxylic acids	C ₅ -C ₁₀	Polyethylene glycol 400	11
	C ₂ -C ₆	Trimeric acid, Ucon LB 550X, tricresyl phosphate	18
		Ucon LB 550X, Carbowax 20M	23
<i>n</i> -Alkyloxiranes	C ₁₃ mono- and dialkyloxiranes		

RESULTS AND DISCUSSION

The anomalies become evident with *n*-alkenes for all of the correlations of the retention data and structure with the number of carbon atoms, no matter whether the contribution of the methylene group to the retention index, I_{CH_2} , of the structural increment, H , of the double-bond position, of the *cis-trans* configuration or of the temperature increment of retention indices is considered².

The value of I_{CH_2} usually increases regularly towards a constant value with increasing number of carbon atoms in a homologous series. In the homologous series with a propyl group, the value of I_{CH_2} for the pair of butyl and propyl derivatives is higher than the expected value^{2,5}. A similar anomaly is evident with the boiling points.

Table II gives the boiling points and the differences in the boiling points for homologous series of *n*-alkanes, *n*-alkenes and *n*-alkylbenzenes. Anomalous features related to the structures of 1-pentene and *n*-propylbenzene obviously occur in comparison with non-anomalous structures of *n*-alkanes (in addition to the effect of even and odd numbers of carbon atoms, which particularly play a role with alkylbenzenes).

The dependence of structural increment, H , on the number of carbon atoms for *n*-alkenes measured on squalane is shown for linear C₃-C₁₄ alkenes in Fig. 1 (left). The anomalous behaviour of 1-pentene, *trans*-2-hexene, *trans*-3-heptene and *trans*-4-octene is obvious. From Fig. 1 (right) it can be seen that the dependence of the difference in the boiling points of *n*-alkenes and *n*-alkanes, δT_b , on the number of carbon atoms in the molecule has a similar course. Hence lower boiling points also correspond to anomalous structures. This can be understood in the following way. On forming a conformer as a consequence of intramolecular interactions, the possibility of the occurrence of intermolecular interactions is decreased, which is reflected in a decreased boiling point of the conformer.

TABLE II

BOILING POINTS AND DIFFERENCES IN BOILING POINTS, δT_b , OF *n*-ALKANES [$\text{CH}_3\text{-(CH}_2\text{)}_n\text{-CH}_3$], 1-ALKENES [$\text{CH}_2\text{=CH-(CH}_2\text{)}_n\text{-CH}_3$] AND *n*-ALKYLBENZENES [$\text{C}_6\text{H}_5\text{-(CH}_2\text{)}_n\text{-CH}_3$]

δT_{b1} is the difference of the boiling points; δT_{b2} is the difference in T_{b1} values.

<i>n</i>	<i>n</i> -Alkanes			<i>l</i> -Alkenes			<i>n</i> -Alkylbenzenes		
	T_b	δT_{b1}	δT_{b2}	T_b	δT_{b1}	δT_{b2}	T_b	δT_{b1}	δT_{b2}
0	-42.07	41.57		-47.70	41.44		110.6		
1	-0.50	36.57	5.00	-6.26	36.23	5.21	136.2	25.6	
2	36.07	32.67	3.90	29.97	34.52	1.71	159.2	23.0	-1.1
3	68.74	29.69	2.98	63.49	30.15	5.37	183.3	24.1	1.9
4	98.43	27.24	2.45	93.64	27.64	2.51	205.5	22.2	1.6
5	125.67	25.13	2.11	121.28	25.29	2.35	226.1	20.6	0.7
6	150.80	23.32	1.81	146.87	23.70	1.59	246.0	19.9	1.5
7	174.12	21.77	1.55	170.57	22.10	1.60	264.4	18.4	0.8
8	195.89			192.67			282.0		

In the homologous series of $\text{H}_2\text{C=CH-(CH}_2\text{)}_n\text{-CH}_3$ type alkenes an anomaly occurs if $n = 2$ provided that the propyl group (with 1-pentene) is attached to the carbon atom next to the double bond. With *n*-alkenes of the $\text{R-CH=CH-(CH}_2\text{)}_n\text{-CH}_3$ type it is necessary to differentiate whether a *trans*- or *cis*-conformation of the alkyl groups on the double bond is present. It can be seen from Fig. 2 that this anomaly

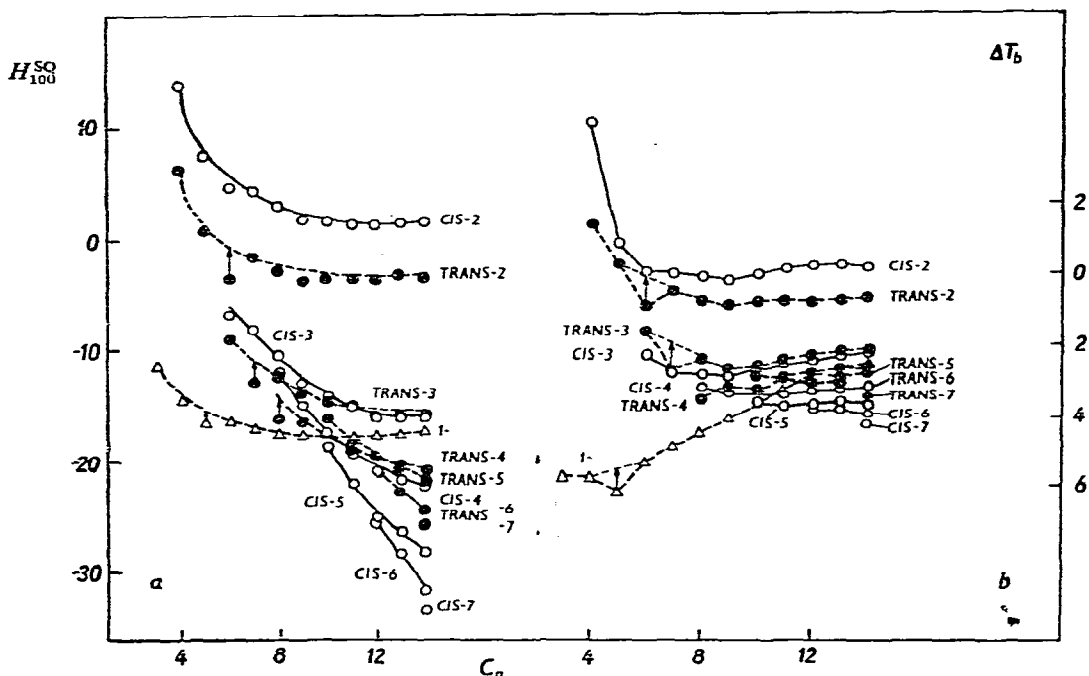


Fig. 1. Dependence of (a) the structural increment on squalane, H^{SQ}_{100} , and (b) the boiling point differences of *n*-alkanes and *n*-alkenes, ΔT_b , on the number of carbon atoms in the molecule ($\text{C}_3\text{-C}_{14}$ *n*-alkenes).

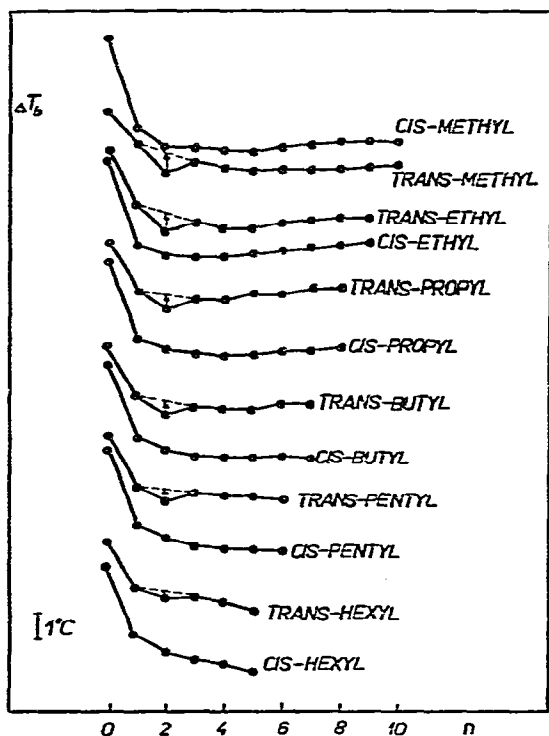


Fig. 2. Dependence of the difference in the boiling points of n -alkanes and n -alkenes, ΔT_b , on the number of methylene groups, n , for alkenes of the type $R-CH=CH-(CH_2)_n-CH_3$.

occurs systematically with *trans*-isomers, and is always greater than the deviation of the corresponding *cis*-isomer.

The value of the deviation caused by the presence of the propyl group decreases with increasing number of carbon atoms in the alkyl group (R) and the differences in the anomalies of *trans*-4- and *cis*-analogues become equal for long alkyl groups, e.g., $R = C_{13}H_{27}$ (Fig. 3). This effect is associated with the removal of structural differences between *cis*- and *trans*-configurations in linear long-chain alkenes.

On separating n -alkenes chromatographically, the anomaly appears most distinctly in the separation of the pair *trans*-4- and *trans*-5-decene. *trans*-4-Decene elutes before *trans*-5-decene on both non-polar and polar stationary phases. This is the only instance with linear alkenes in which the isomer with the double bond nearer the centre of the molecule (5-) is eluted after the isomer with the double bond nearer the end of the molecule (4-). With an increase in the number of carbon atoms, in agreement with the rules for the retention behaviour of isomers⁵, the retention sequence of both isomers gradually changes and for higher n -alkenes the expected sequence of *trans*-4- after *trans*-5-alkene² is observed. With higher n -alkenes the anomalous behaviour of *trans*-4-alkenes appears as their difficult separation from the corresponding *trans*-5-alkenes, e.g., with C_{18} the δI value for the pair *trans*-4-/ *trans*-5- is lower than for the corresponding *trans*-5-/ *trans*-6-, *trans*-6-/ *trans*-7- and *trans*-7-/ *trans*-8- and close to the value for *trans*-8-/ *trans*-9-octadecenes.

The anomalous effect of the propyl group has also been found in the homologous

TABLE III

 $I_{\text{CH}_2}^{100}$ VALUES OF CYCLOALKANES AND CYCLOALKENES ON SQUALANE

Alkyl group	Cyclohexane	Cyclohexene			Cyclopentane	Cyclopentene	
		3-Alkyl-1-	4-Alkyl-1-	1-Alkyl-1-		3-Alkyl-1-	1-Alkyl-1-
Methyl	109.2	109.3	109.1	93.9	107.4	111.4	102.6
Ethyl	92.3	95.0	93.1	86.4	96.2	96.5	87.3
Propyl	97.3	97.3	97.7	96.9	97.8	98.1	99.1
Butyl	99.9	98.7		94.7	99.3	98.8	96.1
Pentyl	99.2	99.9		98.2	98.5	100.4	98.3
Hexyl				99.2	98.6	98.5	99.3
Heptyl							

series of alkylcyclohexenes and alkylcycloheptenes (Table III). The anomaly was observed for 1-propyl-1-cyclohexene. If the propyl group is bound to the carbon atom next to the double bond, *i.e.*, cyclohexenes with alkyl groups in the 2- and 3-positions, no similar deviation was found. The specificity of such a structure is shown by the fact that this anomaly is not found with propylcyclohexane. Identical results were also confirmed during an investigation of alkylcyclopentenes, where anomalous behaviour was shown only by 1-propyl-1-cyclopentene.

The anomaly was similarly confirmed even for conjugated and isolated *n*-dienes if the propyl group was located on the carbon atom next to the double bond. The retention indices of *n*-dienes were calculated from the corresponding structural increments, *H*, of the double bonds in the *n*-alkenes comprising the diene molecule.

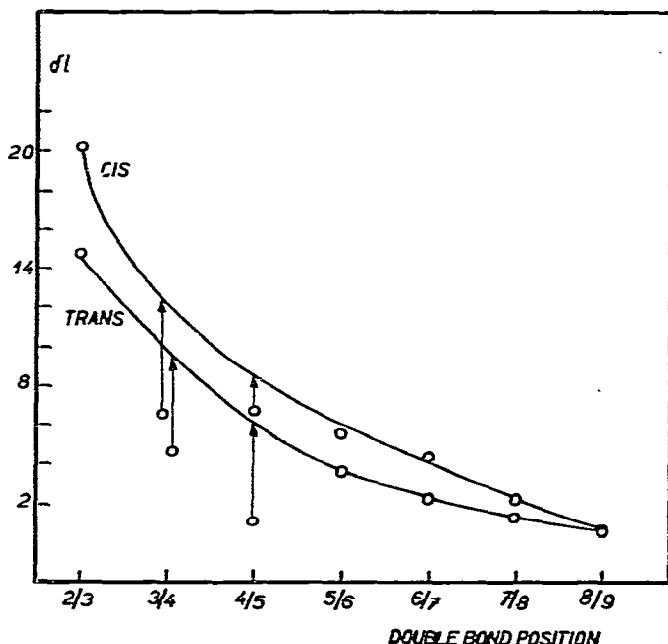


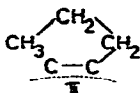
Fig. 3. Dependence of the retention index increment for neighbouring positional *trans*- and *cis*-isomers of *n*-octadecenes on Apiezon L on the double bond position.

For instance, with 1,*trans*-4-heptadiene, the retention index was calculated from the H^{SQ} value for *trans*-3-heptene and 1-heptene. The difference between the measured and calculated retention indices was approximately as great as the value of the anomaly for *trans*-3-heptene as the anomaly is impossible in the molecule of 1,*trans*-4-heptadiene. However with 1,*trans*-4-octadiene the agreement between the calculated and the measured retention indices was better as anomalous structures are found for both *trans*-4-octene and 1,*trans*-4-octadiene¹⁹.

Of other aliphatic hydrocarbons, the anomaly was also confirmed in the homologous series of *n*-alkynes, again with conformations in which the propyl group is bound to the carbon atom next to the triple bond^{3,10}.

A large number of anomalous conformations are possible with alkylbenzenes. In the homologous series of *n*-alkylbenzenes the anomaly was confirmed for *n*-propylbenzene. Anomalous behaviour is similarly observed for propylbenzenes that have one other alkyl group in *o*-, *m*- or *p*-positions. The same is true for polysubstituted propylbenzenes, except for those substituted in two *o*-positions, as demonstrated by comparing the behaviour of 1,2,4-, 1,3,5- and 1,2,3-dimethylalkylbenzenes⁵.

The results suggest that hydrocarbons containing a propyl group bound to the carbon atom next to a double or triple bond or to the benzene ring show an anomalous decrease in the retention indices or in the boiling points. As this deviation was observed with unsaturated hydrocarbons of various structures, the assumption is confirmed that an intramolecular interaction between the propyl group and the π -electron system is concerned. The size of the propyl group makes possible the formation of a cyclic conformer:






This assumption is also confirmed by the fact that if the formation of a cyclic conformation is restricted for steric reasons, the effect of the propyl group is negligible (*cis*-alkenes) or does not appear at all (propylbenzenes substituted in both *o*-positions).

We also tried to differentiate the propyl anomaly as a deviation of the retention indices. The values are shown in Table IV for various π -systems. It can be seen that the value of the anomaly is associated with the intensity of the interaction between the propyl group and the π -system. Electron-donating alkyl groups increase the electron density of the π -system and its interaction with the propyl group is strengthened. The effect appears even more distinctly if the π -system is represented by a conjugated arrangement of multiple bonds. This results in a greater value of the propyl anomaly for conjugated dienes, particularly for alkylbenzenes. An unexpectedly large value of the anomaly was observed for 1-propyl-1-cyclohexene and 1-propyl-1-cyclopentene. This can be explained, to a certain extent, by the better steric capability of the double bond fixed in the ring to form a cyclic conformer with the propyl group. On the other hand, in linear alkenes a very long alkyl chain can sterically hinder the formation of such a conformer, which a decrease of the propyl anomaly with the carbon chain growth. Quantification of the anomalous effect for boiling points suggests that the boiling point of *n*-propylbenzene is decreased by 1.0° and that of 1-pentene by 0.5° as a result of the anomaly (for other types of hydro-

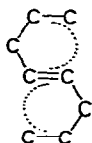
TABLE IV

VALUE OF THE ANOMALY FOR PROPYL DERIVATIVES OF VARIOUS TYPES OF HYDROCARBONS, OBSERVED DURING THEIR SEPARATION ON SQUALANE COLUMN

π -Electron system	Compound	Anomaly (retention index units)
$\text{CH}_2=\text{CH}-$	1-Pentene	1.0
$\text{CH}_3-\text{CH}=\text{CH}-$	<i>trans</i> -2-Hexene	2.8
$\text{C}_2\text{H}_5-\text{CH}=\text{CH}-$	<i>trans</i> -3-Heptene	1.6
$\text{C}_3\text{H}_7-\text{CH}=\text{CH}-$	<i>trans</i> -4-Octene	3.5
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-$	1, <i>trans</i> -4-Octadiene	3.3
$\text{HC}\equiv\text{C}-$	1-Pentyne	1.0
$\text{CH}_3-\text{C}\equiv\text{C}-$	2-Hexyne	2.8
	1-Propyl-1-cyclopentene	5.0
	1-Propyl-1-cyclohexene	5.0
	<i>n</i> -Propylbenzene	4.8

carbons the boiling points known at present are not sufficiently precise for conclusions to be drawn).

The origin of multiple anomalies was also confirmed for structures with more propyl groups in the molecule. A two-fold value of the anomaly⁵ was observed for 1,2-di-*n*-propylbenzene and its sterically "pure" alkyl derivatives. Similarly for *trans*-4-octene, which could consist of a two-ring conformer, the anomaly is greater than that for *trans*-3-heptene, which confirms this assumption.



In accordance with the above results, it must be expected that the value of the anomaly will also be dependent on the polarity of the stationary phase. The value of the anomaly increases for *n*-propylbenzene with increasing polarity of the stationary phase: squalane, acetyltributyl citrate, 1,2,3-triscyanoethoxypropane from 4.8 to 5.6 and to 11 retention index units, respectively. It follows that the anomalous conformer has a lower gas chromatographic polarity than the corresponding hydrocarbon with a non-anomalous structure. This effect can be explained by hindering effects of the twisted propyl group on the sorbate-sorbent interaction. In agreement with this the separation of *trans*-4- and *trans*-5-decenes is also somewhat easier in the above sequence on a non-polar stationary phase (squalane) than a more polar one as the relative decrease in the polarity of anomalous *trans*-4- compared with *trans*-5-decene leads to a decrease in specific interactions and thus also to a decrease in the retention of *trans*-4- compared with *trans*-5-decene; *vice versa*, with higher *n*-alkenes where the retention sequence of the pairs of isomers is reversed (*trans*-5- eluted before *trans*-4-alkenes), the separation is, for the above reasons, somewhat better on polar stationary phases²⁰.

TABLE V

 I_{CH_2} AND δT_b VALUES FOR *n*-CARBOXYLIC ACIDS

Acid	Trimeric acid: $I_{\text{CH}_2}^{140}$	Ucon LB 550X: $I_{\text{CH}_2}^{145}$	Tricresyl phosphate: $I_{\text{CH}_2}^{120}$	δT_b	pK_a^{25}
Acetic	107	98	99	22.6	4.76
Propionic	98	96	93	22.4	4.88
Butyric	110	106	113	22.9	4.82
Valeric	104	105	108	18.6	4.86
Caproic					4.85

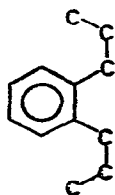
The assumption that the effect of the propyl group will appear even when a hetero-atom is present in the π -electron system was also verified. A comparison of the retention indices or boiling points showed that the propyl anomaly appeared in the homologous series of *n*-alkanoic acids (Table V) and methyl alkyl ketones and acyl chlorides (Table VI).

TABLE VI

BOILING POINTS (T_b) AND THE DIFFERENCES OF BOILING POINTS (δT_b) OF METHYL ALKYL KETONES [$\text{CH}_3\text{-CO-(CH}_2)_n\text{-CH}_3$] AND OF ACYL CHLORIDES [$\text{CH}_3\text{-(CH}_2)_n\text{-COCl}$]

<i>n</i>	Methyl alkyl ketones			Acyl chlorides		
	T_b	δT_{b1}	δT_{b2}	T_b	δT_{b1}	δT_{b2}
0	56.2	23.8		51	29	
1	80	22.3	-1.5	80	22	-7
2	102.3	25.7	3.4	102	25.2	3.2
3	128	23.2	-2.5	127.2	25.8	0.6
4	151.2	21.8	-1.4	153	22	-3.8
5	173	22.3	0.5	175	20.6	-1.4
6	195.3			195.6	19.8	-0.8
7				215.4		

Tight cyclic structures have also been known to possess a similar character to that of π -systems. On comparing the retention indices of *n*-tridecenes and the corresponding dialkyloxiranes of the type



on Ucon LB 550X and Carbowax 20M²⁵, the propyl anomaly of the *trans*-4-derivative may appear not to be totally suppressed by the epoxidation as the retention index of *trans*-4-tridecene did not increase to the value of the anomaly after the epoxidation (Table VII).

TABLE VII

δI VALUES OF THE NEIGHBOURING POSITIONAL ISOMERS OF *n*-TRIDECENES AND THEIR EPOXIDES ON CARBOWAX 20M AND UCON LB 550X

Double bond position	I_{125}^{CW}		I_{125}^{UCON}	
	Alkene	Epoxide	Alkene	Epoxide
<i>trans</i> -2-/ <i>trans</i> -3-	14.4	13.6	12.7	10.8
<i>trans</i> -3-/ <i>trans</i> -4-	5.9	7.4	5.7	5.0
<i>trans</i> -4-/ <i>trans</i> -5-	0.7	1.9	0.5	1.4
<i>trans</i> -5-/ <i>trans</i> -6-	1.3	1.3	1.2	1.1
<i>cis</i> -2-/ <i>cis</i> -3-	21.8	23.2	20.5	19.3
<i>cis</i> -3-/ <i>cis</i> -4-	5.4	11.6	5.8	9.6
<i>cis</i> -4-/ <i>cis</i> -5-	4.5	5.6	4.2	4.4
<i>cis</i> -5-/ <i>cis</i> -6-	2.2	2.6	2.6	2.3

It is known that not only the boiling points but also other physical properties can depend on the conformation. It has been shown that the surface tension and the dielectric constant of *n*-propylbenzene have anomalous values¹¹, and that butyric acid has a dissociation constant lower than those of the neighbouring propionic and valeric acids. An anomaly is also observed for the rate constants, *e.g.*, the enthalpy of isomerization is higher for anomalous *trans*-4-tridecene than for the neighbouring *trans*-3- and *trans*-5-tridecenes²³. It must be mentioned, however, that with regard to fine character of the anomalies, differences in the properties will appear only if the precision of the measurements is sufficiently high.

CONCLUSIONS

Precise gas chromatographic measurements are capable of revealing fine anomalies caused by specific steric conformations of molecules.

Anomalies in the gas chromatographic behaviour were observed for all the classes of investigated hydrocarbons (*n*-alkenes, cycloalkenes, *n*-alkynes, *n*-alkadienes, *n*-alkylbenzenes), for compounds with tight cyclic structures (dialkylloxiranes) and always for compounds with structures that facilitate ring conformation of the propyl group. The results confirm to a great extent the original assumption² that the intramolecular interaction between the propyl group and the π -electron system of the remainder of the molecule leading to the cyclic conformer is the reason for the anomalies with unsaturated hydrocarbons. This phenomenon seems to be a general characteristic of compounds with the structures described above, and it can be called the propyl anomaly or propyl effect.

The propyl anomaly is reflected in a lower retention index, a lower gas chromatographic polarity and a lower boiling point. It will even be apparent in varying reaction rates.

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