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TOPOLOGICAL ANALYSIS OF THE BEHAVIOUR OF LINEAR ALKENES UP TO TETRADECENES IN GAS-LIQUID CHROMATOGRAPHY ON SQUALANE

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SUMMARY

DARC topological analysis (DTA) has been applied to Kováts retention indices for a series of 84 linear alkenes up to tetradecenes studied by gas-liquid chromatography on squalane at 100 °C. The topology-information diagram gives information at the skeletal carbon atom level of the alkene molecules. Very small structural effects are detected and discussed on a statistical basis. This set of *n*-alkenes constitutes a good model for testing the interpretative and physico-chemical potentialities of DTA in order to establish a set of precise reference data for higher *n*-olefins of petrochemical interest.

INTRODUCTION

In petrochemistry, much attention has been devoted to the catalytic dehydrogenation of *n*-alkanes in order to make optimal use of all of the crude oil cut¹. This dehydrogenation gives a mixture of unsaturated hydrocarbons in which *n*-alkenes are the major and the most interesting components. These *n*-alkenes include all possible positional and geometric isomers with a number of carbon atoms corresponding to the respective *n*-alkanes.

The properties of these isomers are very similar and therefore they can only be separated by high-performance capillary gas chromatography. The problem of identifying individual isomers has been solved particularly on squalane^{2,3}. Even for lower *n*-alkenes the separation of every isomer may be difficult. When the number of carbon atoms increases the number of possible isomers increases rapidly. The series of *n*-alkenes from 2 to 20 carbon atoms includes 181 compounds. The greater the

chain length and the more central the position of the carbon-carbon double bond, the more difficult is the separation of these positional isomers. For example, the total separation ($R \neq 1.5$) of *cis*-9- from *cis*-8-octadecene and of *trans*-9- from *trans*-8-octadecene requires high-performance capillary columns which should have about $5 \cdot 10^6$ theoretical effective plates⁴. Such separations are beyond the possibilities of contemporary gas chromatography.

With more polar phases (Carbowax 20M) the separation of these particular positional isomers encounters similar difficulties⁴. Nevertheless, when the polarity of the stationary phase increases, the *cis* isomer is retained more than its corresponding *trans* isomer. Since 1972, the limits of systematic studies of higher *n*-alkenes have been refs. 2, 3, 5, 6 and are still being pushed ahead^{4,7}. Thus, the characterization of *n*-hepta- and *n*-octadecenes on apolar and polar phases (hydrocarbon C₈₇, Apiezon L and Carbowax 20M) has recently been carried out⁴ and the characterization of *n*-nona- decenes and *n*-docosenes is under way.

Simultaneously, the development and utilization of data banks⁸ require interpolation and extrapolation of experimental data with appropriate data processing methods. Topological analysis (DTA) based on the concepts of the DARC topological system (DARC stands for Description, Acquisition, Retrieval and Computer-aided design⁹⁻¹¹) has been developed for this purpose^{12,13}. The precision of gas chromatographic data offers a good model for the physico-chemical interpretation of the behaviour of compounds expressed at the carbon atom level^{14,15} to work out specific interactions which represent another exciting and new direction of research for DTA¹⁶.

In this work we have used DTA to analyse and summarize previous experimental data on *n*-alkenes in order to orientate and minimize further experiments with higher unsaturated *n*-alkenes, dienes or branched alkenes of interest in petrochemistry by calculating a set of precise reference data. Further, the *n*-alkene series is one of the simplest from a structural point of view, but corresponding data have been determined with great precision² and very small structural effects can be detected¹⁷. Consequently, this series constitutes a good model for testing the interpretative potentialities of DTA for the physico-chemical exploitation of retention data in gas-liquid chromatography at the skeletal carbon atom level of the alkene molecules.

EXPERIMENTAL

The data used² were determined at 100 °C by high-performance capillary gas chromatography on a stainless-steel capillary column (200 m \times 0.25 mm I.D.) coated with squalane. The reproducibility of the measurements, calculated as the standard deviation, was 0.18 Kováts index (KI) with C₆-C₁₀ *n*-alkenes and 0.10 KI with higher *n*-alkenes. Kováts indices on squalane at 100 °C for lower alkenes (ethene, propene and 1-butene) were taken from Hively and Hinton¹⁸, whereas for *trans*-2-butene, *cis*-2-butene and isomeric pentenes the data were taken from Rijks and Cramers¹⁹.

We used DARC topological analysis, which is particularly adapted for the treatment of chromatographic retention data of linear and branched compounds¹²⁻¹⁶, but which can also be used for this simple model. This method agrees with the criteria underlined by Soufer²⁰ to define a good method of data processing, that is, simul-

taneous optimization of the number of parameters, the number of compounds used, the precision of the calculation and potential of prediction¹⁹. The correlations were set up by the DARC/PELCO (Perturbation of an Environment Limited Concentric and Ordered) procedure⁹⁻¹¹. The principles of this procedure have already been discussed previously with respect to their applications in chromatography¹². Only certain terms and salient features will be recalled.

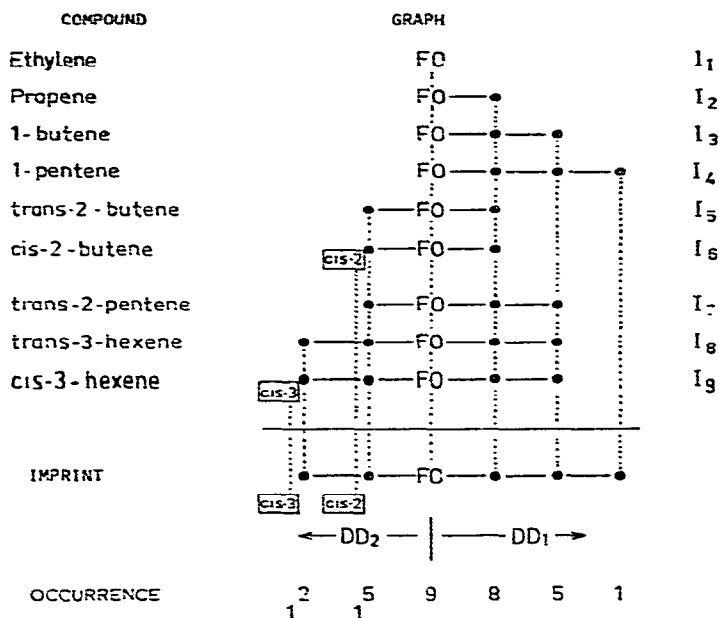


Fig. 1. Principle of superposition of elementary alkene graphs giving an imprint or trace (Tr) characteristic of this set of nine compounds.

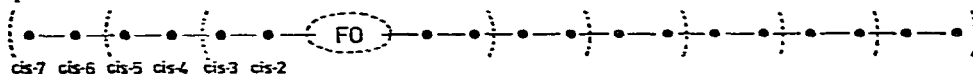
Fig. 1 shows how a set of nine *n*-alkenes ($\text{CH}_2=\text{CH}-\text{R}$, and $\text{R}'-\text{CH}=\text{CH}-\text{R}$) is derived from ethene by progressive and ordered substitution. The pattern $\text{C}=\text{C}$ is taken as the focus. A graph is associated with each of these linear alkenes. The topological sites correspond to the nodes of the graph. Here these nodes correspond to the skeletal carbon atoms of the alkene molecules. Superposition of these elementary graphs gives the characteristic imprint or trace of this set of compounds.

The two development directions DD_1 and DD_2 are non-equivalent because the graphs are ordered. DD_1 is the priority direction, corresponding to lengthening of the alkyl chain R in 1-alkenes $\text{CH}_2=\text{CH}-\text{R}$ and in $\text{R}'-\text{CH}=\text{CH}-\text{R}$ with $\text{R} \geq \text{R}'$. A 180° rotation of the graph of *trans*-2-pentene, in Fig. 1, would be in contradiction with the convention of DD_1 precedence. *Cis* isomers are identified relative to the corresponding *trans* isomers by a supplementary parameter labelled *cis*. In Fig. 1 the occurrence of the focus, topological sites and *cis* parameters is indicated.

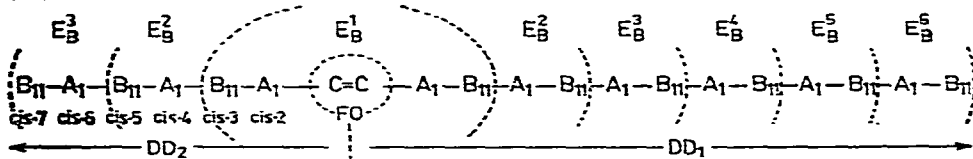
Fig. 2a gives the imprint, also called trace (Tr) on generation grounds¹⁰, of the 84 alkenes listed in Table I. The generation order of all sites is expressed by the

concept of an "Environment that is Limited Concentric and Ordered" (ELCO). Each site is localized in the ELCO by a linear order labelling A_i or B_j , (Fig. 2b) with $j = i = 1$ in the particular case of n -alkenes. The influence of the site is interpreted as a perturbation term (P). For example, the evaluation of term A_1 in the second environment E_B^2 of the first development direction DD_1 (Fig. 2b) corresponds to the difference between information I_4 and information I_3 in Fig. 1, which are relative to 1-pentene and 1-butene, respectively. Actually, the perturbation term of a site is an average value, and is optimized by using a multiple regression program that takes into account all the members of a given population containing this site. This multiple regression shows the interest of giving the occurrence of every topological site to calculate their contribution on statistical bases. Site A_1 in the above example occurs 75 times in the alkene population studied (Fig. 2c).

a) Imprint



b) ELCO



c) Occurrence

2	8	18	32	50	71	84	83	80	75	68	59	48	35	24	15	8	3	1
1	3	5	7	9	13													

d) Topology-Information diagram

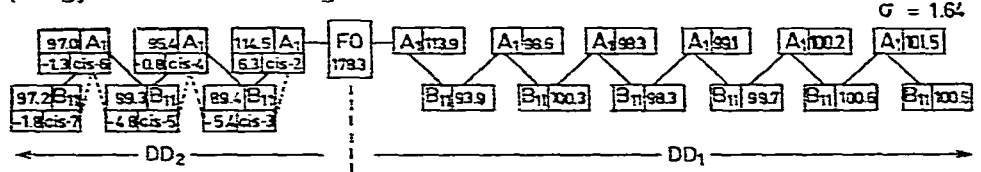


Fig. 2. Organization and distribution of the topological sites. (a) Imprint of the population of 84 n -alkenes obtained by superposition of their corresponding elementary graphs. (b) Organization of molecular environment by the ELCO concept. (c) Occurrence indicates the number of times that each topological site appears when the imprint is determined. (d) Topology-information diagram of the topological analysis of Kováts indices of 84 n -alkenes on squalane at 100°C (this correlation has 25 parameters).

The perturbation terms are the components of vector $\vec{I}(m)$ that characterizes the information for an experimental population made up of m compounds. This vector is defined by the basic topology-information relationship

$$I(\mathcal{E}) = \langle \vec{T}(\mathcal{E}) | \vec{I}(m) \rangle$$

where $I(\mathcal{E})$ is the contribution from the environment to the Kováts index and $\vec{T}(\mathcal{E})$

is the topological vector of the environment $\vec{T}(\mathcal{E}) = (x_1, \dots, X_n)$ with $X_n = 1$ when the n th site of the environment is occupied, and $X_n = 0$ when it is not. The DARC-PELCO method⁹⁻¹¹ consists in calculating the contribution of the focus FO and of the $I(m)$ vector and in defining thereby a topology-information correlation which can be presented as the topology-information diagram of Fig. 2d. The principle of the utilization of such a diagram is given in Fig. 3.

Alkene	1-pentene	trans-2-pentene	cis-3-hexene
Formula	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$
Graph	FO — ● — ● — ●	● — FO — ● — ●	● — ● — FO — ● — ● <u>cis-3</u> <u>cis-2</u>
Topology-information	178.3 113.9 93.9 98.6	114.5 178.3 113.9 93.9	89.4 114.5 178.3 113.9 93.9 -5.4 6.3
Kováts index	calc. 484.7 exptl 482.6	500.6 499.5	590.9 593.3

Fig. 3. Application of the diagram in Fig. 2d to some examples from Fig. 1. We have recalled here a portion of the topology-information diagram useful for these examples.

Calculated Kováts indices with this correlation are compared with experimental Kováts indices in Table I. The corresponding correlation has 25 parameters and the statistical tests are very good: the correlation coefficient is $R = 0.9999$ and the standard deviation is $\sigma = 1.64$. In previous studies on linear and branched alkenes^{12,13,15} we gave only one parameter to characterize the average behaviour of *cis*-alkenes relative to the *trans*-alkenes. By this procedure the correlation is limited to 20 parameters, the correlation coefficient remains practically the same, but the standard deviation increases ($\sigma = 2.78$). The *cis* parameter equals 1.16 KI. With this 20-parameter correlation, estimated Kováts indices and their differences from experimental values are also given in Table I.

RESULTS AND DISCUSSION

Fig. 2d summarizes the behaviour of the 84 alkenes in terms of the contribution of every topological site. It gives the role played by every carbon atom when the chain length increases for every kind of *n*-alkene, *i.e.*, 1-alkenes, *cis*- and *trans*-2-alkenes, etc., up to *cis*- and *trans*-7-alkenes. Fig. 3 explains how such a diagram is used to calculate the Kováts indices of *n*-alkenes which have a graph included in the imprint of the population studied even if the compound had been studied previously or not.

For homologous series, analysts are accustomed to use a graphical exploitation of retention data in the form of linear relationships of Kováts index *versus* the number of carbon atoms. Such a graph will have here about 14 straight parallel lines

TABLE I
 TOPOLOGICAL ANALYSIS OF KOVÁTS INDICES FOR 84 *n*-ALKENES ON SQUALANE
 AT 100 °C.

Parameters of the topology-information correlations having 25 parameters are given in Fig. 3.

No. <i>n</i> -Alkene	Kováts index				
	Exptl. (a)	Calc. (b)	Difference (a) - (b)	Calc. (c)	Difference (a) - (c)
Correlation:					
Number of compounds used		84		84	
Number of parameters		25		20	
Correlation coefficient, R		0.999		0.999	
Standard deviation, σ		1.64		2.78	
1 Ethene	178.30	178.31	-0.01	178.31	-0.01
2 Propene	288.20	292.19	-3.99	292.33	-4.13
3 1-Butene	385.20	386.09	-0.89	386.23	-1.03
4 <i>trans</i> -2-Butene	405.90	406.70	-0.80	409.44	-3.54
5 <i>cis</i> -2-Butene	417.80	413.00	4.79	410.15	7.65
6 1-Pentene	482.60	484.71	-2.11	484.84	-2.24
7 <i>trans</i> -2-Pentene	499.50	500.60	-1.10	503.34	-3.84
8 <i>cis</i> -2-Pentene	505.40	506.91	-1.51	504.06	1.34
9 1-Hexene	583.80	585.02	-1.22	585.16	-1.36
10 <i>trans</i> -3-Hexene	591.10	589.96	1.13	590.08	1.02
11 <i>cis</i> -3-Hexene	593.30	590.90	2.40	590.80	2.51
12 <i>trans</i> -2-Hexene	596.50	599.22	-2.72	601.95	-5.45
13 <i>cis</i> -2-Hexene	604.90	605.52	-0.62	602.67	2.23
14 1-Heptene	683.10	683.36	-0.26	683.50	-0.40
15 <i>trans</i> -3-Heptene	687.40	688.57	-1.17	688.69	-1.29
16 <i>cis</i> -3-Heptene	692.00	689.51	2.49	689.41	2.59
17 <i>trans</i> -2-Heptene	698.70	699.53	-0.83	702.27	-3.57
18 <i>cis</i> -2-Heptene	704.70	705.83	-1.13	702.98	1.72
19 1-Octene	782.60	781.66	0.94	781.80	0.80
20 <i>trans</i> -4-Octene	784.10	783.99	0.11	783.72	0.38
21 <i>cis</i> -4-Octene	788.20	784.15	4.05	784.43	3.77
22 <i>trans</i> -3-Octene	788.20	788.89	-0.69	789.01	-0.81
23 <i>cis</i> -3-Octene	789.80	789.82	-0.02	789.72	0.08
24 <i>trans</i> -2-Octene	797.50	797.89	-0.39	800.61	-3.11
25 <i>cis</i> -2-Octene	803.20	804.17	-0.97	801.32	1.88
26 1-Nonene	882.50	880.80	1.70	880.93	1.57
27 <i>trans</i> -4-Nonene	884.20	884.30	-0.10	884.03	0.17
28 <i>cis</i> -4-Nonene	885.40	884.46	0.94	884.74	0.66
29 <i>trans</i> -3-Nonene	886.40	887.23	-0.83	887.35	-0.95
30 <i>cis</i> -3-Nonene	887.50	888.16	-0.66	888.06	-0.56
31 <i>trans</i> -2-Nonene	896.40	896.17	0.23	898.91	-2.51
32 <i>cis</i> -2-Nonene	901.90	902.47	-0.57	899.62	2.28
33 <i>cis</i> -5-Decene	981.60	978.99	2.61	981.67	-0.07
34 <i>trans</i> -4-Decene	982.50	982.64	-0.14	982.37	0.13
35 1-Decene	982.50	980.48	2.02	980.62	1.88
36 <i>cis</i> -4-Decene	982.80	982.80	-0.00	983.09	-0.29
37 <i>trans</i> -5-Decene	984.10	983.63	0.47	980.96	3.14
38 <i>trans</i> -3-Decene	985.80	985.53	0.27	985.65	0.15
39 <i>cis</i> -3-Decene	985.80	986.46	-0.66	986.36	-0.56
40 <i>trans</i> -2-Decene	996.70	995.31	1.39	998.04	-1.34
41 <i>cis</i> -2-Decene	1001.70	1001.61	0.089	998.76	2.94

TABLE I (continued)

No. <i>n</i> -Alkene	Kováts index					
	Exptl. (a)	Calc. (b)	Difference (a) - (b)	Calc. (c)	Difference (a) - (b)	
Correlation:						
Number of compounds used		84		84		
Correlation coefficient, <i>R</i>		0.999		0.999		
Standard deviation, σ		1.64		2.78		
42	<i>cis</i> -5-Undecene	1078.20	1077.33	0.87	1080.02	-1.82
43	<i>cis</i> -4-Undecene	1080.50	1081.10	-0.60	1081.39	-0.89
44	<i>trans</i> -4-Undecene	1081.10	1080.94	0.16	1080.67	0.43
45	<i>trans</i> -5-Undecene	1081.80	1081.97	-0.17	1079.31	2.50
46	1-Undecene	1082.40	1080.65	1.75	1080.79	1.61
47	<i>cis</i> -3-Undecene	1085.30	1085.60	-0.30	1085.50	-0.20
48	<i>trans</i> -3-Undecene	1085.40	1084.67	0.73	1084.78	0.62
49	<i>trans</i> -2-Undecene	1096.60	1094.99	1.61	1097.73	-1.13
50	<i>cis</i> -2-Undecene	1101.50	1101.30	0.20	1098.44	3.06
51	<i>cis</i> -6-Dodecene	1175.00	1173.02	1.98	1176.36	-1.36
52	<i>cis</i> -5-Dodecene	1175.60	1175.63	-0.03	1178.32	-2.72
53	<i>trans</i> -6-Dodecene	1179.60	1178.98	0.62	1175.65	3.95
54	<i>cis</i> -4-Dodecene	1179.60	1180.24	-0.64	1180.52	-0.92
55	<i>trans</i> -5-Dodecene	1180.60	1180.27	0.33	1177.60	3.00
56	<i>trans</i> -4-Dodecene	1180.60	1180.08	0.52	1179.81	0.79
57	1-Dodecene	1183.00	1181.26	1.74	1181.39	1.61
58	<i>cis</i> -3-Dodecene	1185.10	1185.29	-0.19	1185.18	-0.08
59	<i>trans</i> -3-Dodecene	1185.10	1184.35	0.75	1184.47	0.63
60	<i>trans</i> -2-Dodecene	1196.90	1195.16	1.74	1197.90	-1.00
61	<i>cis</i> -2-Dodecene	1201.70	1201.46	0.24	1198.61	3.09
62	<i>cis</i> -6-Tridecene	1271.20	1271.32	-0.12	1274.66	-3.46
63	<i>cis</i> -5-Tridecene	1273.80	1274.77	-0.97	1277.45	-3.65
64	<i>trans</i> -6-Tridecene	1277.40	1277.28	0.12	1273.95	3.45
65	<i>cis</i> -4-Tridecene	1278.60	1279.92	-1.32	1280.21	-1.61
66	<i>trans</i> -5-Tridecene	1279.50	1279.41	0.09	1276.74	2.76
67	<i>trans</i> -4-Tridecene	1279.90	1279.77	0.13	1279.50	0.40
68	1-Tridecene	1283.10	1282.74	0.36	1281.45	1.65
69	<i>cis</i> -3-Tridecene	1284.40	1285.45	-1.05	1285.35	-0.95
70	<i>trans</i> -3-Tridecene	1284.90	1284.52	0.38	1284.64	0.26
71	<i>trans</i> -2-Tridecene	1297.00	1295.77	1.23	1298.50	-1.50
72	<i>cis</i> -2-Tridecene	1301.60	1302.07	-0.47	1299.22	2.38
73	<i>cis</i> -7-Tetradecene	1366.70	1366.69	0.01	1370.96	-4.26
74	<i>cis</i> -6-Tetradecene	1368.60	1370.45	-1.85	1373.80	-5.20
75	<i>cis</i> -5-Tetradecene	1372.00	1374.45	-2.45	1377.14	-5.14
76	<i>trans</i> -7-Tetradecene	1374.50	1374.49	0.01	1370.25	4.25
77	<i>trans</i> -6-Tetradecene	1375.70	1376.42	-0.72	1373.09	2.61
78	<i>cis</i> -4-Tetradecene	1377.70	1380.09	-2.39	1380.38	-2.68
79	<i>trans</i> -5-Tetradecene	1378.40	1379.09	-0.69	1376.43	1.97
80	<i>trans</i> -4-Tetradecene	1379.30	1379.93	-0.63	1379.66	-0.36
81	1-Tetradecene	1383.20	1383.19	0.01	1383.20	-0.00
82	<i>cis</i> -3-Tetradecene	1384.10	1386.06	-1.96	1385.96	-1.86
83	<i>trans</i> -3-Tetradecene	1384.60	1385.13	-0.53	1385.24	-0.64
84	<i>trans</i> -2-Tetradecene	1396.90	1397.25	-0.35	1398.56	-1.66

for the different sub-populations: reference *n*-alkanes, 1-alkenes and six pairs of *cis*- and *trans*-alkenes from 2-alkenes up to 7-alkenes. Two information contents of Fig. 2d and such a graph in a two-dimensional space would seem similar at first glance. On such a graph only macro-variations due, for example, to the non-linearity of the deviation for the first members of a homologous series could appear. However, micro-variations of about 3 or 4 KI would be lost. For a detailed study it is better to discuss relative variations of small amplitude instead of discussing absolute experimental data. The deviation used will be the isotopology factor, τI (refs. 13 and 14), identical in this case to Schomburg's²¹ homeomorphism factor H^A , that is, to the difference between data relative to an alkene and its isotopological alkane.

Study of the first development direction, DD₁

We must remember that the first development direction, DD₁, according to the well defined law of generation of the topological sites, inside the imprint, corresponds here to lengthening of the *n*-alkyl chain R in compounds CH₂=CH-R or R'-CH=CH-R with R > R'. The contribution of every topological site, determined on statistical bases, is represented more clearly in Fig. 4a, which gives the trend in the variations.

An alternating effect appears up to A₁ in E_B³ (such a site occurs first in 1-heptene for compounds CH₂=CH-R), and after that a regular increase is observed. The most important variations are near the focus. The larger value of 113.9 for site A₁ in E_B¹ in DD₁ expresses the drastic change in the π net charge¹⁵ and dispersion forces brought about by replacing a hydrogen atom at an sp² carbon atom with a methyl group.

This alternating effect is found also when R increases in the 1-alkenes CH₂=CH-R, as is shown by plotting experimental τI values *versus* the carbon number, *n*, of these alkenes (Fig. 4b). From the topology-information diagram (Fig. 2d) it is easy to calculate the contribution of every topological site, $\delta(\tau I)$, to the isotopology factor (τI) of particular compounds. $\delta(\tau I)$ equals the difference between the calculated perturbation term (*P_i*) for a particular site (*S_i*) and 100 KI. To obtain τI for a particular 1-alkene these partial contributions must be added:

$$\tau I = \sum \delta(\tau I)$$

for 1-butene $\tau I = (-21.7) + (13.9) + (-6.1) = -13.9$ KI. These calculated τI values are given *versus* the carbon atom number in Fig. 4b. The curves corresponding to experimental values and calculated values obtained by using the topology-information correlation are closely similar. These variations are also in good agreement with the variation of the vapour pressure of 1-alkenes relative to their isotopological alkanes.

These comparisons show that the perturbation terms associated with every topological site in DD₁ (Figs. 2d and 4a) express adequately the small variations in the observed physico-chemical properties. Differences between the curves in Fig. 4b correspond to differences between experimental and calculated values in Table I. It must be noted that for the heavier alkenes the maximum observed difference is 2 KI, that is, a relative deviation lower than $2 \cdot 10^{-3}$.

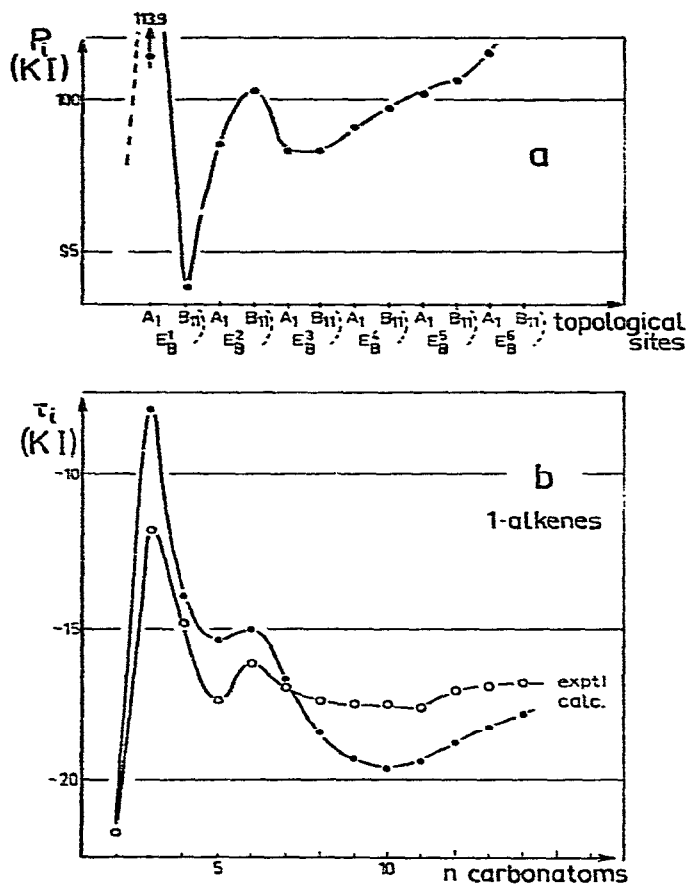


Fig. 4. Influence of chain lengthening in the first development direction, DD_1 . (a) Contribution to the Kováts index of the perturbation term, P_i , associated with every topological site in DD_1 , by lengthening of n -alkyl chain R in $CH_2=CH-R$ or $R'-CH_2=CH-R$ with $R > R'$. (b) τ_i for 1-alkenes ($\tau_i = I_{\text{alkene}} - I_{\text{isotopological alkane}}$) versus number of carbon atoms in every alkene. Comparison of experimental and calculated values. Calculated value for a given alkene corresponds to the sum of elementary contributions of every carbon atom, taken from Fig. 2d.

Study of the second development direction, DD_2

The topological sites in DD_2 are first occupied in the *trans* geometrical isomers from *trans*-2 up to *trans*-7. The average contribution of these topological sites for these isomers is given in Fig. 2d and trends are summarized in Fig. 5a.

The non-equivalence of both development directions DD_1 and DD_2 must be stressed. This non-equivalence reflects the specificity in the behaviour of *trans* and *cis* geometrical isomers relative to the corresponding 1-alkenes.

An alternating effect is also clearly shown in direction DD_2 (Figs. 2d and 5a). The important contribution of site A_1 in E_B^1 (114.5 KI) underlines the great difference between 2-alkenes and 1-alkenes. It shows, once more, the large change in behaviour brought about by replacing a hydrogen atom at an sp^2 carbon atom by a methyl group. But site B_{11} in E_B^1 has a low contribution of only 89.4 KI because the Kováts

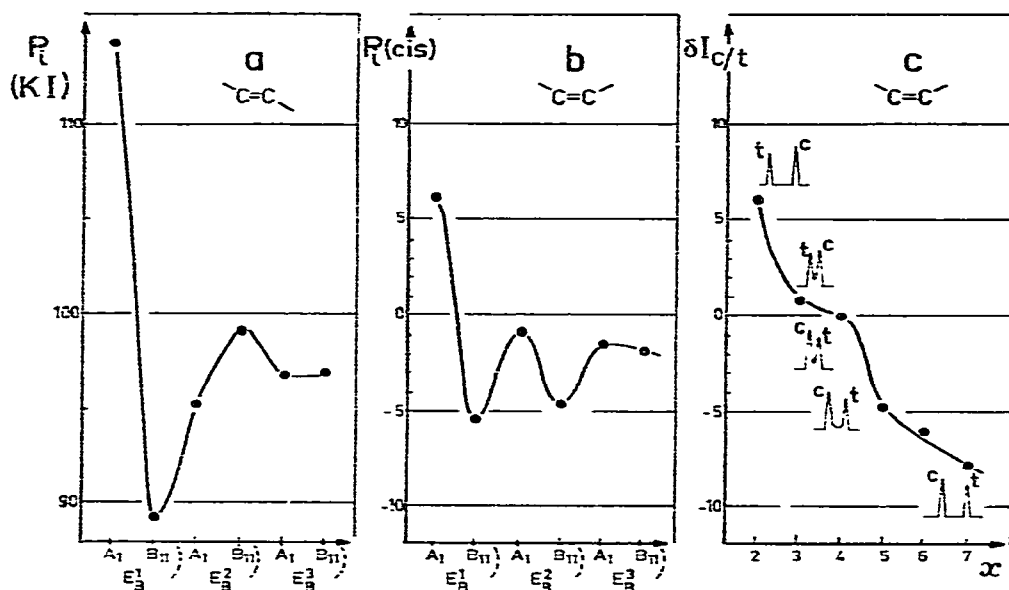


Fig. 5. Statistical behaviour of linear geometrical isomers and contribution of topological sites in the second development direction, DD_2 . (a) Contribution of the sites (P_i) calculated with the *trans*-alkenes; (b) corresponding supplementary parameter, $P_i(cis)$, for *cis*-alkenes; (c) possibilities of separation of different pairs of *cis/trans* isomeric linear x -alkenes for different positions x of the double bond (e.g., $x = 4$ in 4-octene, 4-nonene, ...)

indices of 3-alkenes are systematically lower than those of *trans*-2 alkenes. After this decrease the contributions of topological sites A_1 in E_B^2 (introduced by 4-alkenes) and B_{11} in E_B^2 (introduced by 5-alkenes) increase to 95.4 and 99.3 KI, respectively. Then another decrease is observed for sites A_1 and B_{11} in E_B^3 , introduced by *trans*-6- and *trans*-7-alkenes, respectively.

The perturbation terms associated with the *cis* isomers are calculated relative to the *trans* isomers. They are given in Fig. 2d and corresponding trends are summarized in Fig. 5b. An alternating effect is also evident.

For *cis*-2 alkenes, the positive perturbation term ($P_i = 6.3$ KI) indicates that the Kováts index of *cis*-2 alkenes is about 6.3 KI greater than that for the *trans*-2 alkenes. The *cis* parameter related to B_{11} in E_B^1 is introduced by 3-alkenes, and the corresponding perturbation term decreases markedly, $P_i = -5.4$ KI. This term indicates that Kováts indices of *cis*-3-alkenes are systematically much lower than those of the corresponding *cis*-2-alkenes. However, for *cis*-4-alkenes the difference is less important, only -0.8 KI on average. A large decrease, -4.8 KI, is observed for the *cis*-5-alkenes. A small further decrease is observed for the subsequent *cis*-6- and *cis*-7-alkenes. In Fig. 5b and 5c, the zero values on the ordinate correspond to the contribution of *trans*- n -alkenes, taken as reference compounds.

These perturbation terms, $P_i(cis)$, for the *cis* isomers are defined relative to the *trans* isomers but also to the preceding *cis* isomers, due to the definition of a perturbation term. By making the sum of this elementary contribution, $P_i(cis)$, for every type of *cis* isomer, from *cis*-2 up to *cis*-7 we obtain the values $\delta I_{C/t}$ indicated in Fig. 5c

for every *cis*-alkene. For example, the average behaviour of *cis*-5-alkenes (*c*) defined relative to *trans*-5-alkenes (*t*) only is characterized by:

$$\delta I_{c/t} = \Sigma P_i (cis) = (+ 6.3) + (-5.4) + (-0.8) + (-4.8) = -4.7 \text{ KI}$$

This value corresponds to the average calculated difference between the Kováts indices of *cis*-5-alkenes and *trans*-5-alkenes, by using the topology-information diagram. Fig. 5c, which describes the behaviour of *cis*-*x*-alkenes relative to the *trans*-*x*-alkenes only (with *x* = 2 up to 7), shows clearly the following, on statistical bases:

- (a) the difficulties of separating pairs of *cis*- and *trans*-3- or *trans*-4-alkenes;
- (b) despite chain lengthening, pairs of *cis*- and *trans*-5-, *cis*- and *trans*-6- and *cis*- and *trans*-7-alkenes are easier to separate;
- (c) *cis*-2-alkenes have higher retention times than the corresponding *trans*-2-alkenes, but for heavier alkenes (*cis*-5-, *cis*-6- and *cis*-7-) the reverse is observed, the *cis*-alkenes having lower retention times than the corresponding *trans*-alkenes.

Study of differences between experimental and calculated values for every compound

Differences between the experimental and calculated values (Table I) correspond to the deviation between the real property and the average behaviour calculated on a statistical basis. These differences also show interesting regular trends, which are for the most part understandable even if these differences are taking place in a narrow range of about 3 or 4 KI. These trends are shown in Fig. 6.

The larger deviation observed for 1-propene and *cis*-2-butene underlines the way in which properties of ethene are changed by replacing a hydrogen atom at an sp^2 carbon atom by one and two methyl groups. Nevertheless, part of this relatively abnormal behaviour for the first term of a homologous series is taken into account by the weight attributed to the corresponding perturbation term and has been discussed previously (for example, the experimental Kováts index of *cis*-2-butene is 12 KI higher than that of *trans*-2-butene. Half of this value is accounted for by the *cis* perturbation term associated with A_1 in E_B^1 , in DD_2 . The other half appears in the difference between the experimental and calculated values for this compound).

Molecular symmetry is an important factor and explains the particular behaviour of the first members of a homologous series: *cis*-2-butene, *cis*-3-hexene, *cis*-3-heptene, *cis*-4-octene and *cis*-5-decene. The greatest deviations are observed for these first terms of the corresponding homologous series of geometrical isomers. These deviations do not follow a random distribution but show regular trends. In Fig. 6b, in agreement with previous observations², *trans*-2-hexene deviates from the trend followed by the other *trans*-2-alkenes. This deviation has been attributed to a "propyl effect"¹⁷.

The deviations are greater for the *cis* isomers than for the *trans* isomers (Fig. 6b-e). This difference is due to the fact that the observed τI variations for the *cis* isomers are greater than those for the corresponding *trans* isomers. For example, $\Delta \tau I = 9.6$ KI for *cis*-5-tetradecene and *cis*-5-decene, whereas it is only 5.7 KI for the corresponding *trans* isomers. For the latter the deviations between experimental and calculated values are lower than 1 KI and show that for these *trans*-5-alkenes variation due to increasing chain length is well described by the perturbation term of the

topological sites in DD_1 . The above difference between $\Delta\tau I$ for *cis*-5- and *trans*-5-alkenes explains the observed maximum amplitude of ± 2.5 KI for the differences between the experimental and calculated values (Fig. 6e).

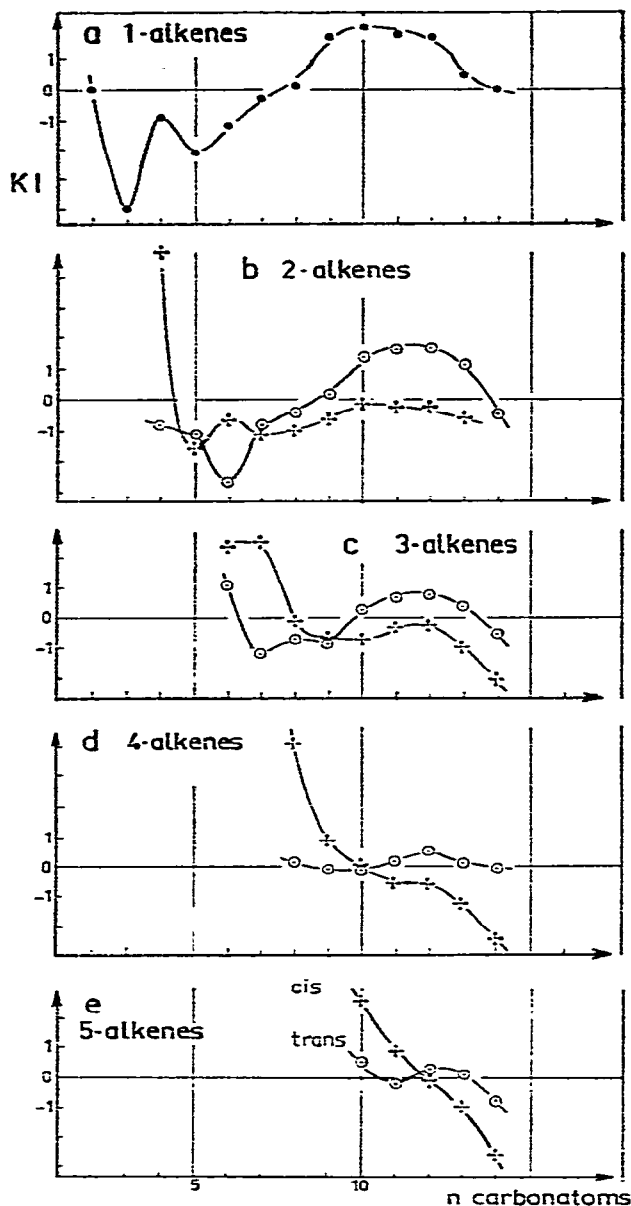


Fig. 6. Study of differences between experimental and calculated Kovats indices of alkenes for homologous series versus their carbon atom number. This shows regular trends for all types of α -alkenes and differentiates well the *cis* and *trans* variations for each group of *cis/trans* isomers as a function of their chain lengthening.

The more central the double bond, the smaller are the differences between the experimental and calculated values for the *trans* isomers, from *trans*-2-alkenes up to *trans*-7-alkenes.

The principles for calculating the contribution of topological sites in the form of an average perturbation term, with the help of multiple regression analysis, are reflected also by the analysis of differences. The smaller differences for *cis*-4- and *cis*-5-alkenes are observed for compounds of average molecular weight. More or less evident similar trends are seen also in Fig. 6a-c.

CONCLUSION

Topological analysis (DTA) based on the DARC topological system summarizes, on a statistical basis, Kováts indices of 84 alkenes for high-performance capillary gas chromatography on squalane. The topology-information diagram gives information at the skeletal carbon atom level of the solute molecules.

As in every mathematical method, our structural model is partly conventional. Use of such a diagram needs a minimum of training which is easily obtained with the help of some examples showing how to calculate Kováts indices for different types of alkenes whose graphs are included in the imprint of the population studied. The results presented in the topology-information diagram and the differences between the experimental and calculated values for every alkene show the trends which have been discussed.

The very precise data used here have been discussed at a second-order level of precision, on statistical bases. These results confirm that the Kováts rule²², stating that every CH₂ group in a homologous series contributes 100 KI, is valid only to a first approximation. From a methodological point of view, when very precise data are used, the present results show the necessity for taking into account the small differences of behaviour between different kinds of *cis*-*x*-alkenes, *i.e.*, for every value of *x*. Retention data of higher *n*-alkenes can be predicted only by structural interpolation in this instance¹².

This model of *n*-alkenes is particularly interesting as a severe test of the analytical and physico-chemical potentialities of DTA. This study shows the links between the well known behaviour of these compounds and the consequences on the contribution of the topological site in the topology-information diagram. It offers a good basis for determining the influence of the polarity at the carbon atom level¹⁴ or for determining if the influence of an apolar stationary phase (squalane, hydrocarbon C₃₇) is limited to a mass effect²³ or if structural effects of the stationary phase also intervene. It would offer also a good basis for the study of long-chain dienes where two double bonds are present in different places and can interact together. Work along these lines in connection with the analysis of unsaturated hydrocarbons of petrochemical interest is currently under way.

REFERENCES

- 1 L. Soják and P. Skalák, *Ropa-Uhlie*, 21 (1979) 485.
- 2 L. Soják, J. Hrivňák, P. Majer and J. Janák, *Anal. Chem.*, 45 (1973) 293.
- 3 L. Soják, J. Hrivňák, I. Ostrovský and J. Janák, *J. Chromatogr.*, 91 (1974) 613.

- 4 L. Soják, J. Krupčík and J. Janák, *J. Chromatogr.*, 195 (1980) 43.
- 5 M. Ryba, *Chromatographia*, 5 (1972) 23.
- 6 O. Eisen, A. Orav and S. Rang, *Chromatographia*, 5 (1972) 229.
- 7 S. Rang, K. Kuningas, A. Orav and O. Eisen, *Chromatographia*, 10 (1977) 55.
- 8 J. C. Bonnet and J. E. Dubois, *Anal. Chim. Acta*, 112 (1979) 245.
- 9 J. E. Dubois, D. Laurent and H. Viellard, *C.R. Acad. Sci., Ser. C*, 263 (1966) 764.
- 10 J. E. Dubois, in A. Balaban (Editor), *The Chemical Applications of Graph Theory*, Academic Press, New York, 1976, p. 330.
- 11 J. E. Dubois, D. Laurent and A. Aranda, *J. Chim. Phys.*, 70 (1973) 1608 and 1616.
- 12 J. E. Dubois and J. Chrétien, *J. Chromatogr. Sci.*, 12 (1974) 811.
- 13 J. R. Chrétien and J. E. Dubois, *J. Chromatogr.*, 126 (1976) 171.
- 14 J. R. Chrétien, *C.R. Acad. Sci., Ser. C*, 281 (1975) 151.
- 15 J. R. Chrétien and J. E. Dubois, *Anal. Chem.*, 49 (1977) 747.
- 16 J. R. Chrétien and J. E. Dubois, *J. Chromatogr.*, 158 (1978) 43.
- 17 L. Soják, P. Zahradnik, J. Leška and J. Janák, *J. Chromatogr.*, 174 (1979) 97.
- 18 R. A. Hively and R. E. Hinton, *J. Gas Chromatogr.*, 6 (1968) 203.
- 19 J. A. Rijks and C. A. Cramers, *Chromatographia*, 7 (1974) 99.
- 20 P. Souter, *J. Chromatogr. Sci.*, 12 (1974) 418 and 424.
- 21 G. Schomburg, *J. Chromatogr. Sci.*, 11 (1973) 151.
- 22 E. Sz. Kováts, *Advan. Chromatogr.*, 1 (1965) 229.
- 23 G. A. Huber and E. Sz. Kováts, *Anal. Chem.*, 45 (1973) 1155.