CHROMSYMP. 421

STUDY OF GAS CHROMATOGRAPHIC BEHAVIOUR OF ALKENES BASED ON MOLECULAR ORBITAL CALCULATIONS

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SUMMARY

Molecular orbital calculations were used to study the gas chromatographic retention of n-alkenes (1-ene, cis- and $trans$-2-, 3-, 4-, 5- and 6-enes). Using the retention index (I), where $I = I_m + I_i$ (I_m = molecular contribution, I_i = solute–stationary phase interaction), the influence of molecular parameters such as total energy (E_T), binding energy (E_b), excess-charge distribution (δ) and values of the energy and coefficients of highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals were considered. E_T and E_b represent the I_m term and E_{HOMO} and HOMO–LUMO interactions, defined by Klopman's equation, are directly related to the I_i term of the retention index. General equations including several homologous series (cis and $trans$ isomers) are presented.

INTRODUCTION

Several workers have studied the gas chromatographic behaviour of alkenes and provided different correlations between the retention index (I) and the molecular structure of these compounds[1–11]. Takács et al.[1] separated the retention index into two additive components: molecular (I_m) and interaction (I_i) contributions. Sanz et al.[2] used an additive calculation method that considered the contribution of the different structural units of molecules. Papazova and Dimov[3,4] predicted I values with the aid of a physico-chemical index (PCI) and a structural number correction. Soják and co-workers[5–7] presented a detailed analytical study on the behaviour of alkenes that considered structural increments such as position of the double bonds, differences between spatial isomers and column temperature. Similar considerations were used by Rang et al.[8]. Chrétien and co-workers[9–11] applied the Darc-Pelco method in their topological analysis of alkenes. This method is partially conventional but it does not assume *a priori* subdivision of the Kováts retention index. Buydens et al.[12] used the complete neglect of differential overlap (CNDO/2) method to correlate I and quantum chemical parameters.

From these papers it is apparent that the Kováts retention index (I) depends on two principal factors: molecular contributions and interactions between the molecule and the stationary phase. These factors were treated by using different parameters and calculation methods.

The purpose of this study was to consider the gas chromatographic behaviour of alkenes as a molecular phenomenon that could be investigated by means of molecular orbital (MO) calculations to establish which electronic and orbital parameters are required for a determination of the retention index.

EXPERIMENTAL

Kováts retention indices (I) of alkenes on squalane (100°C) were taken from Dubois *et al.*[10]. Molecular parameters of orbitals were calculated by the CNDO/2 method (Fig. 1). Lengths and angles of bonds were taken from the *Handbook of Chemistry and Physics*[13]. The coordinate origin was located on a carbon atom of the double bond for all calculations. An example is shown in Fig. 2.
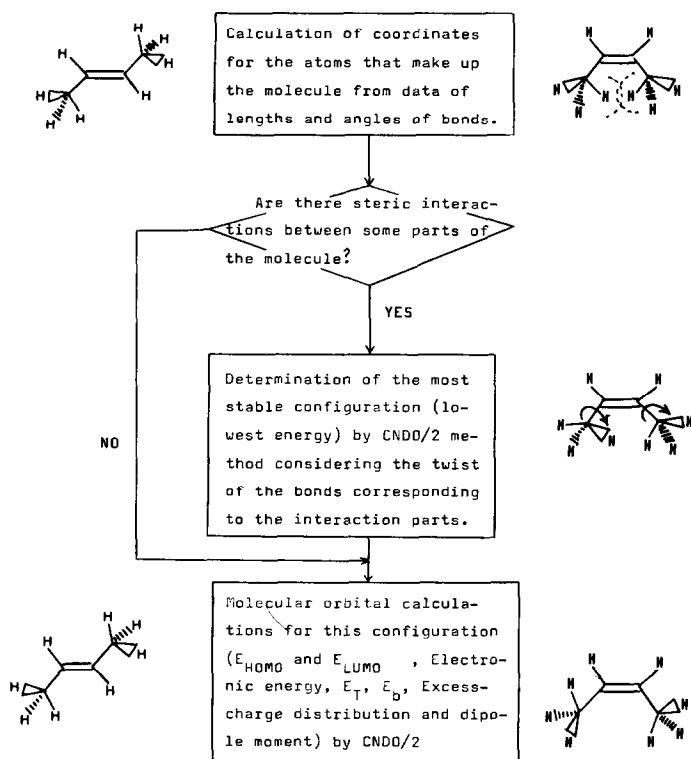

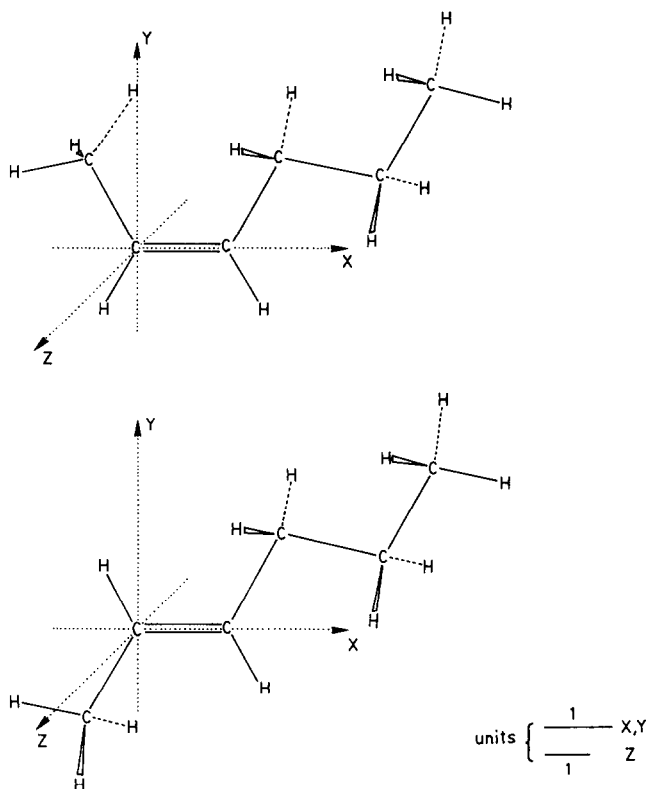Fig. 1. Method of calculating molecular orbital parameters.

Fig. 2. Spatial distribution of different atoms for alkenes. Top: *cis*-2-hexene; bottom: *trans*-2-hexene.

RESULTS AND DISCUSSION

Molecular contribution

To determine which MO magnitudes are directly related to the chromatographic retention of alkenes, total energy (E_T), binding energy (E_b), energy of lowest unoccupied and highest occupied MOs (E_{LUMO} and E_{HOMO}), excess-charge distribution (δ) and the corresponding orbital coefficients of HOMO and LUMO orbitals (C_{HOMO} and C_{LUMO}) were calculated by CNDO/2. The values of these parameters are listed in Table I.

Plots of I vs. E_T or E_b for homologous series yield straight lines with high correlation coefficients (> 0.999) and low standard deviations in all instances. Some examples are shown in Fig. 3. Table II shows the corresponding equations and statistical data.

No significant correlations were found when other parameters (E_{HOMO}, E_{LUMO} and δ) were used, a fact also confirmed by the present authors for several homologous series of esters[14]. Generally, the gas chromatographic retention of alkenes is principally determined by E_T or E_b.

Analysts generally use I vs. molecular parameters for the homologous series listed in Table II. Thus, eleven straight lines are employed. It is possible to obtain

TABLE I

MOLECULAR ORBITAL VALUES OF ALKENES (CNDO/2)

E_T = total energy; E_b = binding energy; E_{HOMO}, E_{LUMO} = energy of highest occupied and lowest unoccupied molecular orbitals; E = interaction energy (Klopman's equation, see eqn. 7).

Compound	E_T	E_b	E_{HOMO}	E_{LUMO}	Coefficient of p_z of LUMO of $C^1 = C^2$		$-\Delta E$	Excess-charge distribution of $C^1 = C^2$	
					C^1	C^2		C^1	C^2
Ethene	− 17.058	− 2.173	−0.5863	0.1976	0.7071	0.7071	−5.061	−0.031	−0.031
Propene	− 25.761	− 3.433	−0.5182	0.1830	0.6665	−0.6447	−4.699	−0.055	0.014
1-Butene	− 34.445	− 4.676	−0.5181	0.1832	0.6660	−0.6442	−5.684	−0.055	0.012
1-Pentene	− 43.130	− 5.917	−0.5180	0.1836	0.6659	−0.6436	−4.671	−0.055	0.010
1-Hexene	− 51.814	− 7.159	−0.5081	0.1841	0.6657	−0.6436	−4.657	−0.055	0.010
1-Heptene	− 60.498	− 8.401	−0.4944	0.1845	0.6657	−0.6437	−4.648	−0.055	0.010
1-Octene	− 69.182	− 9.642	−0.4837	0.1847	0.6656	−0.6439	−4.643	−0.055	0.010
1-Nonene	− 77.866	−10.884	−0.4754	0.1849	0.6656	−0.6439	−4.638	−0.055	0.010
1-Decene	− 86.550	−12.126	−0.4689	0.1850	0.6656	−0.6440	−4.637	−0.055	0.010
1-Undecene	− 95.235	−13.368	−0.4637	0.1850	0.6656	−0.6440	−4.637	−0.055	0.010
1-Dodecene	−103.919	−14.609	−0.4594	0.1851	0.6656	−0.6440	−4.634	−0.055	0.010
1-Tridecene	−112.603	−15.851	−0.4559	0.1851	0.6656	−0.6441	−4.635	−0.055	0.010
1-Tetradecene	−121.287	−17.093	−0.4530	0.1851	0.6657	−0.6440	−4.635	−0.055	0.010
cis-2-Butene	− 34.465	− 4.695	−0.4906	0.1715	0.6189	−0.6189	−4.467	−0.006	−0.006
cis-2-Pentene	− 43.150	− 5.938	−0.4890	0.1722	0.6202	−0.6218	−4.479	−0.006	−0.009
cis-2-Hexene	− 51.834	− 7.179	−0.4889	0.1727	0.6196	−0.6210	−4.456	−0.005	−0.013
cis-2-Heptene	− 60.518	− 8.421	−0.4885	0.1731	0.6194	−0.6211	−4.445	−0.006	−0.013
cis-2-Octene	− 69.202	− 9.663	−0.4882	0.1734	0.6192	−0.6212	−4.437	−0.006	−0.013
cis-2-Nonene	− 77.887	−10.904	−0.4881	0.1736	0.6192	−0.6213	−4.432	−0.006	−0.013
cis-2-Decene	− 86.571	−12.146	−0.4734	0.1738	0.6191	−0.6213	−4.426	−0.006	−0.013

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cis-2-Undecene	− 95.255	− 13.388	−0.4672	0.1739	0.6191	− 0.6214	−4.425	−0.006	−0.013
cis-2-Dodecene	− 103.939	− 14.630	−0.4622	0.1739	0.6191	− 0.6214	−4.425	−0.006	−0.013
cis-2-Tridecene	− 112.623	− 15.871	−0.4582	0.1740	0.6191	− 0.6214	−4.422	−0.006	−0.013
trans-2-Butene	− 34.462	−4.692	−0.4808	0.1691	0.6208	− 0.6208	−4.558	−0.006	−0.006
trans-2-Pentene	− 43.148	− 5.934	−0.4791	0.1698	0.6224	− 0.6236	−4.572	−0.006	−0.010
trans-2-Hexene	− 51.831	− 7.176	−0.4790	0.1703	0.6219	− 0.6229	−4.549	−0.006	−0.014
trans-2-Heptene	− 60.515	− 8.418	−0.4786	0.1707	0.6216	− 0.6229	−4.537	−0.006	−0.014
trans-2-Octene	− 69.199	− 9.660	−0.4783	0.1710	0.6215	− 0.6230	−4.529	−0.007	−0.014
trans-2-Nonene	− 77.883	− 10.901	−0.4778	0.1712	0.6214	− 0.6231	−4.523	−0.007	−0.014
trans-2-Decene	− 86.567	− 12.143	−0.4706	0.1713	0.6213	− 0.6232	−4.521	−0.007	−0.014
trans-2-Undecene	− 95.252	− 13.384	−0.4648	0.1714	0.6213	− 0.6232	−4.518	−0.006	−0.013
trans-2-Dodecene	− 103.936	− 14.626	−0.4603	0.1715	0.6213	− 0.6232	−4.515	−0.007	−0.014
trans-2-Tridecene	− 112.620	− 15.868	−0.4566	0.1715	0.6213	− 0.6233	−4.516	−0.007	−0.014
trans-2-Tetradecene	− 121.304	− 17.110	−0.4535	0.1716	0.6213	− 0.6233	−4.513	−0.007	−0.014
cis-3-Hexene	− 51.835	− 7.179	−0.4869	0.1720	0.6238	− 0.6238	−4.525	−0.010	−0.010
cis-3-Heptene	− 60.519	− 8.422	−0.4868	0.1724	0.6232	− 0.6230	−4.504	−0.010	−0.013
cis-3-Octene	− 69.203	− 9.663	−0.4864	0.1729	0.6229	− 0.6230	−4.533	−0.010	−0.013
cis-3-Nonene	− 77.887	− 10.904	−0.4861	0.1732	0.6228	− 0.6231	−4.481	−0.010	−0.013
cis-3-Decene	− 86.571	− 12.147	−0.4814	0.1734	0.6227	− 0.6232	−4.476	−0.010	−0.013
cis-3-Undecene	− 95.255	− 13.388	−0.4736	0.1735	0.6227	− 0.6233	−4.474	−0.010	−0.013
cis-3-Dodecene	− 103.940	− 14.630	−0.4674	0.1736	0.6227	− 0.6233	−4.472	−0.010	−0.013
cis-3-Tridecene	− 112.624	− 15.871	−0.4624	0.1737	0.6226	− 0.6234	−4.469	−0.010	−0.013
cis-3-Tetradecene	− 121.308	− 17.114	−0.4584	0.1737	0.6226	− 0.6234	−4.469	−0.010	−0.013
trans-3-Hexene	− 51.832	− 7.177	−0.4776	0.1705	0.6251	− 0.6251	−4.584	−0.010	−0.010
trans-3-Heptene	− 60.516	− 8.419	−0.4775	0.1710	0.6246	− 0.6244	−4.561	−0.010	−0.014
trans-3-Octene	− 69.200	− 9.660	−0.4771	0.1714	0.6243	− 0.6244	−4.549	−0.010	−0.013
trans-3-Nonene	− 77.884	− 10.902	−0.4768	0.1717	0.6242	− 0.6245	−4.541	−0.011	−0.014
trans-3-Decene	− 86.568	− 12.144	−0.4729	0.1719	0.6241	− 0.6246	−4.535	−0.011	−0.013
trans-3-Undecene	− 95.252	− 13.385	−0.4670	0.1720	0.6241	− 0.6247	−4.533	−0.011	−0.013
trans-3-Dodecene	− 103.936	− 14.627	−0.4622	0.1721	0.6240	− 0.6247	−4.530	−0.011	−0.013

TABLE I (*continued*)

| Compound	E_T	E_b	E_{HOMO}	E_{LUMO}	Coefficient of p_z of LUMO of $C^1 = C^2$		$-\Delta E$	Excess-charge distribution of $C^1 = C^2$	
					C^1	C^2		C^1	C^2
trans-3-Tridecene	−112.621	−15.869	−0.4582	0.1722	0.6240	−0.6247	−4.527	−0.011	−0.013
trans-3-Tetradecene	−121.305	−17.111	−0.4549	0.1722	0.6240	−0.6247	−4.527	−0.011	−0.013
cis-4-Octene	− 69.203	− 9.663	−0.4867	0.1729	0.6224	−0.6224	−4.481	−0.013	−0.013
cis-4-Nonene	− 77.887	−10.905	−0.4863	0.1733	0.6221	−0.6224	−4.468	−0.013	−0.013
cis-4-Decene	− 86.571	−12.146	−0.4860	0.1736	0.6220	−0.6225	−4.461	−0.014	−0.013
cis-4-Undecene	− 95.255	−13.388	−0.4812	0.1738	0.6219	−0.6226	−4.456	−0.014	−0.013
cis-4-Dodecene	−103.940	−14.630	−0.4734	0.1739	0.6219	−0.6239	−4.454	−0.014	−0.013
trans-4-Octene	− 69.200	− 9.660	−0.4775	0.1714	0.6239	−0.6239	−4.542	−0.014	−0.013
trans-4-Nonene	− 77.884	−10.902	−0.4771	0.1718	0.6236	−0.6239	−4.529	−0.014	−0.013
trans-4-Decene	− 86.568	−12.144	−0.4749	0.1721	0.6234	−0.6240	−4.521	−0.014	−0.013
trans-4-Undecene	− 95.252	−13.385	−0.4689	0.1723	0.6234	−0.6241	−4.516	−0.014	−0.013
trans-4-Dodecene	−103.936	−14.627	−0.4639	0.1725	0.6233	−0.6242	−4.511	−0.014	−0.013
cis-5-Decene	− 86.571	−12.147	−0.4859	0.1737	0.6222	−0.6222	−4.457	−0.013	−0.013
cis-5-Undecene	− 95.255	−13.388	−0.4856	0.1740	0.6220	−0.6223	−4.449	−0.013	−0.013
cis-5-Dodecene	−103.940	−14.630	−0.4809	0.1742	0.6220	−0.6224	−4.445	−0.013	−0.013
cis-5-Tridecene	−112.624	−15.872	−0.4732	0.1744	0.6219	−0.6224	−4.439	−0.014	−0.013
trans-5-Decene	− 86.568	− 12.144	−0.4755	0.1723	0.6236	−0.6236	−4.514	−0.014	−0.014
trans-5-Undecene	− 95.252	−13.385	−0.4700	0.1725	0.6235	−0.6237	−4.509	−0.014	−0.014
trans-5-Dodecene	−103.936	−14.627	−0.4652	0.1727	0.6234	−0.6238	−4.503	−0.014	−0.014
trans-5-Tridecene	−112.621	−15.869	−0.4611	0.1729	0.6233	−0.6239	−4.498	−0.014	−0.013
cis-6-Dodecene	−103.940	−14.630	−0.4853	0.1743	0.6221	−0.6221	−4.441	−0.013	−0.013
cis-6-Tridecene	−112.624	−15.872	−0.4806	0.1745	0.6221	−0.6222	−4.436	−0.013	−0.013
cis-6-Tetradecene	−121.308	−17.113	−0.4731	0.1746	0.6220	−0.6223	−4.434	−0.014	−0.013
trans-6-Dodecene	−103.936	−14.627	−0.4657	0.1728	0.6236	−0.6236	−4.501	−0.014	−0.014
cis-6-Tridecene	−112.621	−15.869	−0.4619	0.1730	0.6235	−0.6237	−4.496	−0.014	−0.014
trans-6-Tetradecene	−121.305	−17.110	−0.4585	0.1731	0.6234	−0.6237	−4.492	−0.014	−0.014
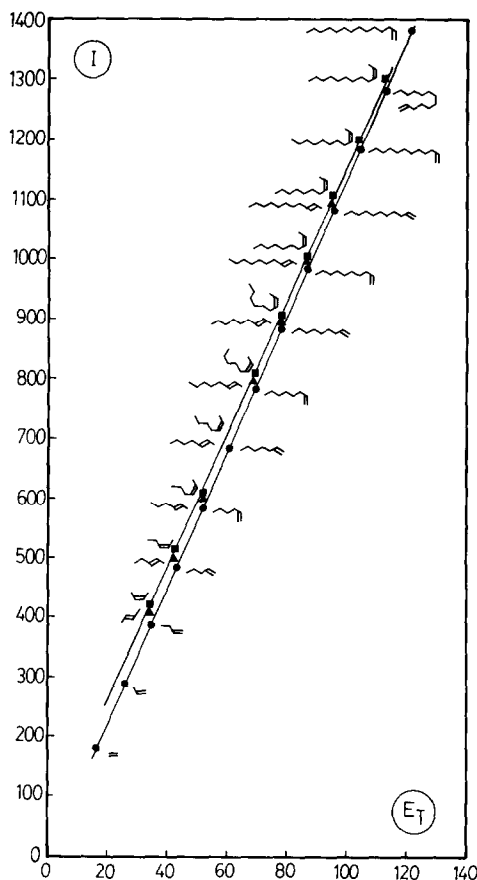
Fig. 3. Plots showing straight lines of I vs. E_T corresponding to different homologous series of n-alkenes. ●, 1-enes; ■, cis-2-enes; ▲, trans-2-enes.

general equations by using total energy (one for 1-enes and another one for all cis- and trans-alkene isomers). Thus, E_T or E_b could represent the general chromatographic behaviour of alkenes, because different homologous series can be described by a single equation:

1-enes:
$$I = -11.509\ E_T - 13.069 \tag{1}$$
($N = 13, r = 1.0000, s = 2.20, F = 376008.58$)

cis- and trans-alkenes:
$$I = -11.250\ E_T + 15.142 \tag{2}$$
($N = 62, r = 0.9995, s = 8.06, F = 66470.55$)

or

1-enes:
$$I = -80.454\ E_b + 7.475 \tag{3}$$
($N = 13, r = 1.0000, s = 1.95, F = 480314.52$)

TABLE II

I vs. *E*$_b$ AND *I* vs. *E*$_T$ EQUATIONS AND STATISTICS

N = Number of compounds employed; *r* = correlation coefficient; *s* = standard deviation; *F* = experimental value of Snedecor test.

Compounds	Equation	N	r	s	F
1-Enes	$I = -80.454E_b + 7.474$	13	1.0000	1.95	480314.52
cis-2-Enes	$I = -79.560E_b + 36.284$	10	0.9999	3.55	64077.30
trans-2-Enes	$I = -80.105E_b + 24.803$	11	1.0000	2.28	208554.75
cis-3-Enes	$I = -79.490E_b + 19.118$	9	0.9994	9.80	6104.23
trans-3-Enes	$I = -79.916E_b + 13.402$	9	0.9995	8.90	7465.15
cis-4-Enes	$I = -78.755E_b + 26.695$	5	1.0000	0.68	207690.52
trans-4-Enes	$I = -79.721E_b + 14.396$	5	1.0000	0.51	377926.81
cis-5-Enes	$I = -78.441E_b + 28.402$	4	1.0000	0.54	163823.16
trans-5-Enes	$I = -79.327E_b + 20.429$	4	1.0000	0.42	272262.79
cis-6-Enes	$I = -77.930E_b + 34.757$	3	1.0000	0.56	59160.99
trans-6-Enes	$I = -78.977E_b + 24.307$	3	1.0000	0.24	344155.51
1-Enes	$I = -11.509E_T - 13.069$	13	1.0000	2.20	376008.58
cis-2-Enes	$I = -11.416E_T + 15.564$	10	0.9999	4.18	46147.70
trans-2-Enes	$I = -11.454E_T + 6.007$	11	1.0000	2.26	213535.11
cis-3-Enes	$I = -11.379E_T + 2.422$	9	1.0000	1.16	439070.21
trans-3-Enes	$I = -11.437E_T - 3.548$	9	1.0000	1.00	587727.94
cis-4-Enes	$I = -11.261E_T + 8.453$	5	1.0000	0.68	209430.45
trans-4-Enes	$I = -11.399E_T - 4.299$	5	1.0000	0.52	358941.46
cis-5-Enes	$I = -11.215E_T + 10.263$	4	1.0000	0.57	148226.80
trans-5-Enes	$I = -11.147E_T + 1.912$	4	1.0000	0.46	231555.41
cis-6-Enes	$I = -11.147E_T + 16.187$	3	1.0000	0.49	78086.33
trans-6-Enes	$I = -11.291E_T + 5.988$	3	1.0000	0.20	461463.52

cis- and trans-alkenes:
$$I = -78.661 \, E_b + 32.946 \tag{4}$$
$(N = 62, r = 0.9994, s = 9.47, F = 48164.18)$

In our opinion, eqns. 2 and 4 have an interesting physico-chemical significance, but for analytical purposes the equations indicated in Table II or calculated by other workers[2–7,10] may be more practical.

Solute–stationary phase interactions

The second factor determining the retention index value is the interaction factor. Electronic parameters, such as charge density (δ), have no significant influence on the interaction factor, because the calculated values (CNDO/2) for all carbon and hydrogen atoms of each compound are virtually zero and are very similar.

This interaction factor could be studied from MO calculations, considering interactions between HOMO or LUMO orbitals, because these are the principal determinants of physico-chemical interactions of the different alkenes with the stationary phase.

These interactions can be studied by means of Klopman's equation[15,16]:

$$-\Delta E = \frac{2\Sigma C^2_{HOMO}C^2_{LUMO}\beta^2}{E_{HOMO} - E_{LUMO}} \tag{5}$$

where C_{HOMO} = coefficient of HOMO, C_{LUMO} = coefficient of LUMO, β = overlapping integral, E_{HOMO} = energy of HOMO, E_{LUMO} = energy of LUMO and $-\Delta E$ = interaction energy.

Two possibilities may be considered. First, interaction between HOMO of the alkene and LUMO of the stationary phase; this is not possible, because different atomic orbitals appear, depending on the alkene. Thus, for example, in *trans*-2-butene only the p_z orbital has significance, whereas in *trans*-2-nonene s, p_x and p_y orbitals should be considered (see Table III).

TABLE III

HOMO COEFFICIENTS OF SOME $C^1 = C^2$ ALKENES

Compound	HOMO of C^1				HOMO of C^2			
	s	p_x	p_y	p_z	s	p_x	p_y	p_z
trans-2-Butene	0.000	0.000	0.000	−0.568	0.000	0.000	0.000	−0.568
trans-2-Heptene	0.000	0.000	0.000	−0.552	0.000	0.000	0.000	−0.551
trans-2-Nonene	−0.048	−0.182	−0.128	0.000	0.067	0.239	0.194	0.000
cis-2-Hexene	0.000	0.000	0.000	0.566	0.000	0.000	0.000	0.563
cis-2-Decene	−0.049	−0.143	−0.106	0.000	0.068	0.204	0.164	0.000
cis-3-Octene	0.000	0.000	0.000	0.552	0.000	0.000	0.000	0.553
cis-3-Undecene	−0.049	−0.145	−0.104	0.000	0.067	0.206	0.162	0.000
trans-3-Decene	0.024	0.216	0.160	0.000	−0.054	−0.253	−0.202	0.000
trans-4-Octene	0.000	0.000	0.000	0.536	0.000	0.000	0.000	0.536
trans-4-Decene	0.006	0.256	0.195	0.000	−0.038	−0.277	−0.219	0.000
cis-4-Decene	0.000	0.000	0.000	−0.554	0.000	0.000	0.000	−0.553
cis-5-Undecene	0.000	0.000	0.000	0.554	0.000	0.000	0.000	0.554
trans-5-Decene	−0.017	0.279	0.217	0.000	−0.017	−0.279	−0.217	0.000
cis-6-Dodecene	0.000	0.000	0.000	−0.554	0.000	0.000	0.000	−0.554
trans-6-Tridecene	0.009	−0.249	−0.184	0.000	0.024	0.256	0.192	0.000

Second, interaction between LUMO of the alkene and HOMO of the stationary phase, which appears more useful because for all alkenes only the p_z orbital of the two carbon atoms of a C = C moiety has values different from zero (see Table I), and Klopman's equation can therefore be applied. The values of $-\Delta E$ for $C^1 = C^2$ alkenes, where

$$-\Delta E = \frac{2\beta^2(C^2_{LUMO\ of\ C^1} + C^2_{LUMO\ of\ C^2})}{-E_{LUMO}} \qquad (6)$$

or

$$-\Delta E \propto \frac{C^2_{LUMO\ of\ C^1} + C^2_{LUMO\ of\ C^2}}{-E_{LUMO}} \text{ (in } 2\beta^2 \text{ units)} \qquad (7)$$

are listed in Table I. The conventional values C_{HOMO} = 1 and E_{HOMO} = 0 for the stationary phase are assigned in these calculations.

TABLE IV

EXPERIMENTAL AND CALCULATED (FROM EQN. 8) I VALUES

Compound	I_{exp}	$I_{calc.}$	Error (%)
cis-2-Butene	417.8	413.5	1.03
cis-2-Pentene	505.4	506.9	0.30
cis-2-Hexene	604.9	604.5	0.07
cis-2-Heptene	704.7	700.4	0.61
cis-2-Octene	803.2	795.6	0.95
cis-2-Nonene	901.9	890.1	1.31
cis-2-Decene	1001.7	1002.1	0.04
cis-2-Undecene	1101.5	1103.1	0.15
cis-2-Dodecene	1201.7	1202.6	0.07
cis-2-Tridecene	1301.6	1301.4	0.02
trans-2-Butene	405.9	409.7	0.94
trans-2-Pentene	499.5	502.9	0.68
trans-2-Hexene	596.5	600.4	0.65
trans-2-Heptene	698.7	696.5	0.31
trans-2-Octene	797.5	791.7	0.73
trans-2-Nonene	896.4	886.9	1.06
trans-2-Decene	996.7	989.3	0.74
trans-2-Undecene	1096.6	1090.2	0.58
trans-2-Dodecene	1196.9	1189.6	0.61
trans-2-Tridecene	1297.0	1287.4	0.74
trans-2-Tetradecene	1396.9	1385.1	0.84
cis-3-Hexene	593.3	595.2	0.32
cis-3-Heptene	692.0	692.4	0.06
cis-3-Octene	789.8	781.5	1.05
cis-3-Nonene	887.5	884.2	0.37
cis-3-Decene	985.8	984.2	0.16
cis-3-Undecene	1085.3	1087.3	0.18
cis-3-Dodecene	1185.1	1188.5	0.29
cis-3-Tridecene	1284.4	1288.5	0.34
cis-3-Tetradecene	1384.1	1386.8	0.20
trans-3-Hexene	591.1	596.2	0.86
trans-3-Heptene	687.4	693.7	0.92
trans-3-Octene	788.2	789.8	0.20
trans-3-Nonene	886.4	885.0	0.16
trans-3-Decene	985.8	984.2	0.16
trans-3-Undecene	1085.4	1085.1	0.03
trans-3-Dodecene	1185.1	1184.8	0.02
trans-3-Tridecene	1284.9	1283.6	0.10
trans-3-Tetradecene	1384.6	1381.1	0.25
cis-4-Octene	788.2	789.9	0.22
cis-4-Nonene	885.4	886.2	0.09
cis-4-Decene	982.8	981.3	0.16
cis-4-Undecene	1080.5	1081.3	0.07
cis-4-Dodecene	1179.6	1184.5	0.42
trans-4-Octene	784.1	790.5	0.82
trans-4-Nonene	884.2	886.7	0.28
trans-4-Decene	982.5	984.2	0.17
trans-4-Undecene	1081.1	1085.7	0.43
trans-4-Dodecene	1180.6	1186.0	0.50
cis-5-Decene	981.6	982.0	0.04
cis-5-Undecene	1078.2	1077.3	0.08

TABLE IV (continued)

Compound	I_{exp}	$I_{calc.}$	Error (%)
cis-5-Dodecene	1175.6	1177.1	0.13
cis-5-Tridecene	1273.8	1280.8	0.54
trans-5-Decene	984.1	984.7	0.06
trans-5-Undecene	1081.8	1085.6	0.35
trans-5-Dodecene	1180.6	1185.8	0.44
trans-5-Tridecene	1279.5	1285.1	0.44
cis-6-Dodecene	1175.0	1172.5	0.21
cis-6-Tridecene	1271.2	1272.5	0.10
cis-6-Tetradecene	1368.6	1375.3	0.48
trans-6-Dodecene	1179.6	1185.6	0.50
trans-6-Tridecene	1277.4	1284.4	0.55
trans-6-Tetradecene	1375.7	1382.7	0.51
		Average:	0.41

On the other hand, as can be seen in Table I, E_{HOMO} has significantly different values for alkenes of different homologous series and could also be considered to be related to these interactions. The equations I vs. E_T and $-\Delta E$ and I vs. E_T and E_{HOMO} reduce the standard deviation of eqn. 2 slightly, but if we consider these two factors jointly ($-\Delta E$ and E_{HOMO}) a large reduction in standard deviation results. This indicates that both parameters are directly related to the phenomenon of interaction between the alkenes and the stationary phase.

The equation for cis and trans isomers is

$$I = -10.772\,E_T + 169.035\,(-\Delta E) + 1184.236\,E_{HOMO} + 1378.317 \qquad (8)$$
$$(N = 62,\ r = 0.9999,\ s = 4.66,\ F = 187611.79)$$

This is the most general equation representing the chromatographic retention of alkenes accurately (see Table IV). The first term ($-10.772\,E_T$) includes the molecular factor and the others represents the solute–stationary phase interactions.

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