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# Chromatographic Identification of (*E*)- and (*Z*)-Isomers of Unsaturated Organic Compounds Using Their Physicochemical Characteristics

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**Abstract**—The values of physicochemical properties determine completely the sequence of chromatographic elution of (*Z*)- and (*E*)-isomers of 1,2-disubstituted unsaturated compounds and can therefore be used as reference data for their GC-identification. The isomer with the minimum boiling point, relative density, and refractive index has the least retention parameters. By the ratio of the values of these properties the (*Z*)- and (*E*)-isomers form two groups: (*Z*) > (*E*) and (*Z*) < (*E*). This feature is due to the larger polarity of the (*Z*)-isomers of asymmetrically substituted compounds containing polar substituents at the double bond C=C. The discovered regularities may be extended to the *cis*- and *trans*-isomers of 1,2-disubstituted cycloalkanes and even to the position isomers of substituted arenes.

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One of the challenges of the chromatography-mass spectrometric identification of trace organic compounds (when their preparative isolation and, therefore, the use of NMR spectroscopy are impossible) is to establish the structure of the carbon skeleton of the isomeric molecules. The standard mass spectra of many structural isomers are only slightly different from each other, therefore generally such problem is solved by the involvement of chromatographic retention parameters, especially the retention index (RI) possessing the greatest inter-laboratory reproducibility. In the absence of reference RI values they can be estimated from the values of the fundamental physicochemical properties of organic compounds [1].

Among these tasks, an important one may be selected, which is not yet considered in the literature, namely, the identification of (*E*)- and (*Z*)-isomers of unsaturated compounds (π-diastereomers). Its main features are as follows:

– With a few exceptions, the standard mass spectra of electron impact of (*E*)- and (*Z*)-isomers are almost identical [2], hence the detection of these analytes requires interpretation of the chromatographic retention parameters;

– In various samples such isomers are often found simultaneously, except the case of their formation in stereospecific reactions (e.g., the presence of individual isomers is typical for natural compounds);

– If a sample contains all possible (*E*)- and (*Z*)-isomers, their unequivocal identification is sufficiently attained by the prediction of the sequence of their chromatographic elution [3] (at the "before–after" level). If only a part of the possible isomers is detected, then the solution of this task requires the use of absolute retention parameters thus becoming more complicated.

This paper estimates the possibility of identification of (*E*)- and (*Z*)-isomers of simple unsaturated organic compounds based on the interpretation of their basic physicochemical properties (including the normal boiling point, relative density, and refractive index). As the simplest compounds of this type the isomers can be considered containing one 1,2-disubstituted C=C double bond. In the presence in the structure of $N$ multiple C=C bonds the number of isomers in the case of asymmetric structures increases to $2^N$, and for symmetric, up to 3 ($N$ = 2), 6 ($N$ = 3), 10 ($N$ = 4), 20 ($N$ = 5), etc.

In considering this problem, two points are worth mentioning. The first complicates the solution. For objective reasons (incorrect assignment of the isomers, impossibility of checking because of the unavailability of individual substances, the effect of the special structural features, etc.) the assignment of isomers based on increase of their retention parameters sometimes does not correspond to that expected from the values of their physicochemical properties. The second point concerns other types of isomers, first of all σ-diastereomers. Now only sporadic attempts are known of the prediction of the sequence of their gas chromatographic elution [4]; the same is true for the *cis*- and *trans*-isomers of cyclic structures. The search for possible approaches to the identification of the simplest (*E*)- and (*Z*)-isomers should be seen as a major prerequisite for the successful solution of these more complex problems.

The necessity to formulate the general rules for predicting the order of chromatographic elution of (*E*)- and (*Z*)-isomers is due to the fact that reliable values of retention indices of both isomers are known simultaneously only for the simplest of homologs of different series. The same concerns the values of physicochemical properties. If the unambiguous assignment of isomers is impossible, then often their sequence number at the elution is indicated, like "isomer no. 1," "isomer no. 2," etc. Thus, to obtain the most reliable conclusions about the correlation of physicochemical properties and the chromatographic parameters it is necessary to consider the simplest pairs of (*E*)- and (*Z*)-isomers. It is important to note that the method of calculation of RI for such isomers does not exist to date. So, one of the known versions of additive schemes [5] used in the database [6] provides equal estimated RI values for (*E*)- and (*Z*)-isomers.

**Table 1.** Physicochemical parameters and chromatographic retention indices of (*E*)- and (*Z*)-isomers of some 1,2-disubstituted unsaturated compounds

| Compound (molecular weight) | Isomer | $T_b$, °C | $d_4^{20}$ | $n_D^{20}$ | RI[a] |
|---|---|---|---|---|---|
| I. $T_b$, RI (*Z*) > $T_b$, RI (*E*) | | | | | |
| 2-Butene (56) | *E* | 0.9 | 0.62 | 1.38 | 407±3 |
| | *Z* | 3.7 | 0.64 | 1.39 | 418±6 |
| 1,3-Pentadiene (68) | *E* | 42.0 | 0.676 | 1.430 | 521±8 |
| | *Z* | 44.1 | 0.691 | 1.436 | 533±7 |
| 2-Pentene (70) | *E* | 36.4 | 0.648 | 1.379 | 507±4 |
| | *Z* | 36.9 | 0.656 | 1.383 | 513±4 |
| 1-(1-Propenyl)oxirane (84) | *E* | 101–102 | 0.872 | 1.438 | 696±10 |
| | *Z* | 103–104 | 0.895 | 1.438 | 702±10 |
| 1,2-Dimethoxyethylene (88) | *E* | 94 | – | – | – |
| | *Z* | 101 | – | – | – |
| 3-Ethyl-2-penten-3-yne (94) | *E* | – | – | – | 707 |
| | *Z* | – | – | – | 725 |
| 1,5-Heptadiene (96) | *E* | 94 | – | – | 685±4 |
| | *Z* | – | – | – | 690 |
| 1,2-Dichloroethylene (96)[b] | *E* | 40 | 1.255 | 1.446 | 551±14 |
| | *Z* | 60 | 1.287 | 1.450 | 596±11 |
| 5-Methyl-2-hexene (98) | *E* | 88.1 | 0.701 | 1.400 | 668±3 |
| | *Z* | 89.5 | 0.699 | – | 678±4 |
| 4-Methyl-3-hexene (98) | *E* | 93.5 | – | – | 691±3 |
| | *Z* | 95.4 | – | – | 699±4 |
| 3-Hexen-1-ol (100) | *E* | 152–153.5 | – | – | 847±7 |
| | *Z* | 156 | – | – | 854 |
| 2-Methyl-3-chloropropenoic nitrile (101) | *E* | 126–128 | 1.076 | 1.457 | – |
| | *Z* | 155–158 | 1.092 | 1.458 | – |

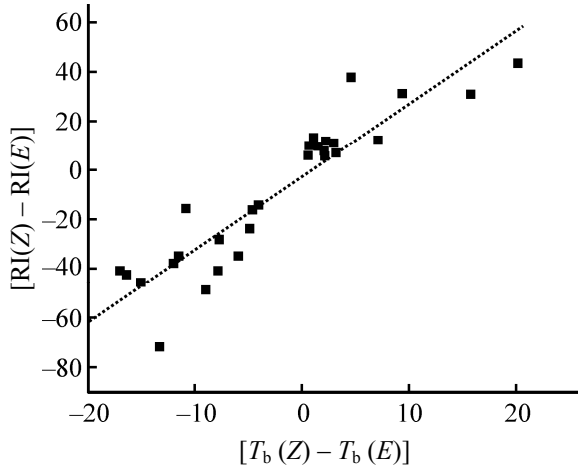
**Table 1.** (Contd.)

| Compound (molecular weight) | Isomer | $T_b$, °C | $d_4^{20}$ | $n_D^{20}$ | RI[a] |
|---|---|---|---|---|---|
| I. $T_b$, RI (*Z*) > $T_b$, RI (*E*) | | | | | |
| 1,4-Octadiene (110) | *E* | – | – | – | 769 |
| | *Z* | – | – | – | 772 |
| 2,5-Octadiene (110) | 2*E*,5*E* | – | – | – | 789 |
| | 2*E*,5Z | – | – | – | 790 |
| | 2*Z*,5Z | | | | 795 |
| 2,6-Octadiene (110) | 2*E*,6*E* | – | – | – | 799 |
| | 2*E*,6Z | – | – | – | 804 |
| | 2*Z*,6Z | – | – | – | 808 |
| 1,2-Dichloropropene (110) | *E* | 76.9 | 1.182 | 1.447 | 738±13 |
| | *Z* | 92.5 | 1.187 | 1.454 | 770±14 |
| 2-Nonene (126) | *E* | 150.1 | – | – | 902±2 |
| | *Z* | 150.8 | – | – | 912±2 |
| 3-Phenylpropenoic nitrile (129) | *E* | 249 | 1.029 | 1.584 | – |
| | *Z* | 263.8 | 1.030 | 1.603 | 1233 |
| 2-Butenylbenzene (132) | *E* | 183–184 | 0.886 | 1.508 | 1053±7 |
| | *Z* | – | 0.890 | 1.524 | 1071 |
| 2,6-Dimethyl-2 ,4,6-octatriene (alloocymene) (136) | *E* | 188–192 | 0.814 | – | 1118±3 |
| | *Z* | 196–198 | 0.817 | – | 1131±3 |
| 1-Bromo-2-chloroethylene (140) | *E* | 75.3 | – | – | 627 |
| | *Z* | 84.6 | 1.78 | – | 659 |
| 3-Hexenyl acetate (142) | *E* | – | – | – | 974±2 |
| | *Z* | – | – | – | 990±9 |
| 3,6-Dimethyl-1,3-octadien-5-one (tagetone) (152) | *E* | – | – | – | 1129±6 |
| | *Z* | – | – | – | 1138±4 |
| Methyl 4-octenoate (156) | *E* | – | – | – | 1096±3 |
| | *Z* | – | – | – | 1118±4 |
| 2-Dodecene (168) | *E* | 215.5 | 0.761 | 1.433 | 1202±2 |
| | *Z* | 216.5 | 0.765 | 1.434 | 1215±6 |
| 1,2-Dibromoethylene (184) | *E* | 108 | 2.267 | 1.550 | 734±2 |
| | *Z* | 112.5 | 2.285 | 1.543 | 762±6 |
| 2-Pentadecene (210) | *E* | 270.2 | – | – | 1500±2 |
| | *Z* | 270.6 | – | – | 1510±2 |
| II. $T_b$, RI (*Z*) < $T_b$, RI (*E*) | | | | | |
| 3-Penten-1-yne (66) | *E* | 51.9 | 0.727 | 1.438 | 578±14 |
| | *Z* | 44 | 0.727 | 1.437 | 537±8 |
| 2-Butenoic nitrile (67) | *E* | 121 | 0.822 | 1.418 | 716±11 |
| | *Z* | 107.7 | 0.820 | 1.422 | 644 |
| 2-Butenal (70) | *E* | – | – | – | 678 |
| | *Z* | 103 | 0.852 | 1.437 | 636±16 |

**Table 1.** (Contd.)

| Compound (molecular weight) | Isomer | $T_b$, °C | $d_4^{20}$ | $n_D^{20}$ | RI[a] |
|---|---|---|---|---|---|
| II. $T_b$, RI (*Z*) < $T_b$, RI (*E*) | | | | | |
| 1-Chloropropene (76) | *E* | 37 | 0.935 | 1.405 | 510±5 |
| | *Z* | 32.8 | 0.935 | 1.406 | 495±7 |
| 2-Methyl-2-butenoic nitrile (81) | *E* | 138.2 | 0.831 | 1.432 | 723 |
| | *Z* | 123.1 | 0.823 | 1.424 | 677±8 |
| 2-Pentenoic nitrile (81) | *E* | 144 | 0.827 | 1.427 | 737 |
| | *Z* | 127 | 0.821 | 1.421 | 696 |
| 1-Methoxy-1-butene (86) | *E* | 76.7 | – | – | – |
| | *Z* | 72 | – | – | – |
| 2-Pentyl-1-ol (86) | *E* | 139.1 | 0.847 | 1.434 | 762±8 |
| | *Z* | 137.8 | 0.853 | 1.435 | – |
| 2-Chloro-1-butene (90) | *E* | 68.1 | 0.920 | 1.422 | 606±2 |
| | *Z* | 63.5 | 0.915 | 1.419 | 590±3 |
| 2-Chloro-2-butene (90) | *E* | 70.6 | 0.924 | 1.424 | 617±4 |
| | *Z* | 62.8 | 0.914 | 1.419 | 589±5 |
| 2-Ethyl-2-butenoic nitrile (95) | *E* | 156 | 0.832 | 1.436 | 815 |
| | *Z* | 139.5 | 0.823 | 1.428 | 772 |
| Ethyl 2-butenoate (114) | *E* | 136.5 | 0.917 | 1.424 | 825±4 |
| | *Z* | 129–130 | 0.925 | 1.426 | – |
| 1-Propenylbenzene (118) | *E* | 178.3 | 0.906 | 1.551 | 1010±11 |
| | *Z* | 167.4 | 0.902 | 1.543 | 994±14 |
| 1-Butenylbenzene (132) | *E* | 198.7 | 0.901 | 1.541 | 1105±7 |
| | *Z* | 187.1 | 0.898 | 1.528 | 1070±7 |
| 2-Chloroethenylbenzene (138) | *E* | 197–199 | 1.111 | 1.573 | 1030±7 |
| | *Z* | – | – | – | 1000±8 |
| 1,2,3-Trichlorpropene (144) | *E* | 149 | 1.429 | 1.498 | 895±9 |
| | *Z* | 137 | 1.402 | 1.500 | 857±9 |
| 1-Pentenylbenzene (146) | *E* | 211–212 | 0.902 | 1.532 | 1205±4 |
| | *Z* | 202–203 | 0.876 | 1.515 | 1156±3 |
| Propyl 1-propenyl disulfide (148) | *E* | – | – | – | 1110 |
| | *Z* | – | – | – | 1102±2 |
| 3,7-Dimethyl-2,7-octadienal (152) | *E* | 228–229 | 0.891 | 1.488 | 1253±11 |
| | *Z* | 220–225 | 0.868 | 1.516 | 1218±8 |
| 3,7-Dimethyl-2,7-octadienol (154) | *E* | 230 | 0.886 | 1.478 | 1240±11 |
| | *Z* | 224–226 | 0.885 | 1.478 | 1216±5 |
| β-Isopropoxystyrene (162) | *E* | – | – | – | 1274 |
| | *Z* | – | – | – | 1252 |
| Methyl cynnamate (162) | *E* | 262 | – | – | 1357±11 |
| | *Z* | – | – | – | 1291 |
| Ethyl cynnamate (176) | *E* | – | 1.049 | 1.560 | 1444±13 |
| | *Z* | | | | 1364 |
| Cynnamyl acetate (176) | *E* | – | 1.054 | 1.560 | 1424±11 |
| | *Z* | – | – | – | 1376 |
| 1-Iodo-2-chloroethylene (188) | *E* | 116–119 | 2.219 | 1.583 | – |
| | *Z* | 113–114 | 2.105 | 1.572 | – |

[a] A dash means no data known; some values of retention indices are reported without standard deviations; [b] Here and hereinafter for Cl- and Br-containing compounds the molecular weights corresponds to the mass numbers of light isotopes of the halogens ($^{35}Cl$ and $^{79}Br$).




Correlation of differences of chromatographic retention indices of (*Z*) - and (*E*)-isomers with the differences in their normal boiling points. Linear regression parameters: $\Delta RI = a\Delta T_b + b$: *a* 3.0±0.2; *b* –1.3±2.4; *r* 0.917; $S_0$ 12.

Moreover, modern methods of coding chemical structures by means of molecular graphs [7] mostly are not suitable for (*Z*)- and (*E*)-isomers.

Table 1 compares the values of the basic physicochemical properties (normal boiling point, relative density, and refractive index) and RI values of (*E*)- and (*Z*)-isomers of some unsaturated compounds with 1,2-disubstituted C=C double bonds. For some compounds the data are unknown, which is typical for information systems both in organic chemistry and chromatography. The most important feature of the problem, as reflected the structure of Table. 1, is that there are both compounds for which the boiling point of (*Z*)-isomer is higher than that of (*E*)-isomer (27 pairs of isomers in the first part of Table 1.), and the compounds with the $T_b(Z) < T_b$(E ) (25 pairs of isomers in the second part of Table 1). For further discussion, the first group compounds can be tentatively classified as having "normal" $T_b(Z)/T_b(E)$ ratio, and the second group as having "reverse" ratio. However, to reach better results in the discussion of this important feature it is useful to discuss it a little later (see below).

An equally important feature of any pair of (*Z*)- and (*E*)-isomer is that in all cases the sequence of their chromatographic elution uniquely corresponds to the successive increase in their boiling points, which in the presence of reference $T_b$ values allows a prediction of the order of release of isomers from the chromatographic column. This rule should be viewed as a special case of a more general pattern, which determines the elution order of any structural isomers [3] and forms the basis of their chromatographic identification. It should be noted that this law cannot be explicitly found in the modern manuals on gas chromatography (see, for example, [8, 9]), which, of course, should be corrected.

A more rigorous description of the dependence $\Delta RI = RI(Z) - RI(E)$ vs. $\Delta T_b = T_b(Z) - T_b(E)$ for different classes of compounds using a single linear regression equation is impractical due to the low value of the correlation coefficient ($r$ = 0.917). Plot of this dependence shown in the figure illustrates a significant spread of points, but confirms one-to-one correspondence of signs of the quantities ΔRI and $\Delta T_b$ [sign(ΔRI) = sign($\Delta T_b$)], that is, full compliance of the order of their elution sequence and the $T_b$ values. Moreover, since the value of the coefficient $b$ in absolute value is less than its standard deviation ($b$ = –1.3±2.4), hence it is not statistically significant and, therefore, plot $\Delta RI \approx a\ \Delta T_b + b$ passes through the origin. This is consistent with the obvious fact that at the equal boiling points of (*E*)- and (*Z*)-isomers ($\Delta T_b \approx 0$) they cannot be separated by chromatography ($\Delta RI \approx 0$). If $T_b$ of isomers are not equal, the first eluted is always the isomer with a lower boiling point.

An interesting feature of the predictions of the elution of isomers is a possiblity to use for this purpose not $T_b$, but the properties like relative density ($d_4^{20}$) and refractive indices ($n_D^{20}$).

It is known that the chromatographic retention of analytes on nonpolar phases is mainly determined by two factors: the intensity of their dispersion interactions with the stationary phase and their boiling points. Energy of dispersive (van der Waals) interactions is proportional to the electron polarizability of analyte molecules (α) [10], which, in turn, is proportional to their molar refraction ($MR_D$):

$$MR_D = (M_r/d_4^{20})[(n_D^{20})^2 - 1]/[(n_D^{20})^2 + 2] \sim N_A\alpha, \qquad (1)$$

where $M_r$ is the molecular weight, $d_4^{20}$ is the relative density, $n_D^{20}$ is the refractive index, $N_A$ is Avogadro's number.

A distinctive feature of the isomers of any type (both structural and σ- and π-diastereomers) is the close values of their molar refraction, the difference do not exceed, as a rule, the errors in their determination (~ ±0.2 $cm^3\ mol^{-1}$). Despite the obviousness of this fact, it is expedient to confirm it by an example of some of the compounds listed in Table 2.

**Table 2.** Molecular refraction of some compounds

| Compound | Isomer | $MR_D$, $cm^3$ $mol^{-1}$ |
|---|---|---|
| 2-Methyl-3-chloropropenoic nitrile | *E* | 25.7 |
| | *Z* | 25.4 |
| 1,2-Dibromoethylene | *E* | 26.1 |
| | *Z* | 25.7 |
| 2-Pentenoic nitrile | *E* | 25.2 |
| | *Z* | 25.0 |
| 1-Pentenylbenzene | *E* | 50.2 |
| | *Z* | 50.3 |

**Table 3.** Physicochemical characteristics of (*E*)- and (*Z*)-isomers of 1,2-dichloroethylene and 1-propenylbenzene[a]

| Compound (molecular weight) | Isomer | $T_b$, °C | $d_4^{20}$ | $n_D^{20}$ | RI |
|---|---|---|---|---|---|
| 1,2-Dichloroethylene (96) | *E* | 40 | 1.255 | 1.446 | 551±14 |
| | ***Z*** | **60** | **1.287** | **1.450** | **596±11** |
| 1-Propenylbenzene (118) | ***E*** | **178.3** | **0.906** | **1.551** | **1010±11** |
| | *Z* | 167.4 | 0.902 | 1.543 | 994±14 |

[a] The entries containing the highest values of all of these characteristics simultaneously are printed in bold.

Hence, at the minor differences between the molar refraction the cause of inequality of retention indices of any isomers, including (*E*) and (*Z*) isomers, is the above discussed difference in their boiling points. However, due to the problem in question, it is interesting to assess the reason of the difference in the boiling points of isomers, since these physicochemical characteristics are also related to the intensity of intermolecular interactions. The inequality of $T_b$ of the isomers is not consistent with the similarity in their molar refraction, and therefore, with the small difference in the energies of intermolecular interactions.

The cause of this discrepancy is simple enough. From the data in Table 1 it follows that all isomers having higher boiling points have a higher density. Consequently, at the equality of their molar refraction and therefore ofthe energies of their local intermo-lecular interactions, the specific values of energy (per unit volume of material) are different. To compensate the significant effect of the higher density of one of the isomers on its molar refraction [Eq. (1)], it possesses a larger value of the refractive index. In other words, the density decreases with increasing molar volume, which leads to an increase in the energy of molecular interactions. Given the unusual nature of this conclusion, it is also useful to illustrate it in more detail by the example of some data from Table 1, included into Table 3 .

For example, for 1,2-dichloroethylene (first part of Table 1) the difference in $T_b$ of the isomers is 20°C [(*Z*) > (*E*)]. In parallel with the higher $T_b$ value the (*Z*)-isomer is characterized by a higher density, (1.287) compared to (*E*)-isomer (1.255) and the higher value of the refractive index (1.450 compared to 1.446). In the case of 1-propenylbenzene the $T_b$ ratio of the isomers is reverse: the $T_b$ of (*Z*)-isomer is less by 11°C, but this is reflected in an equally lower density [0.902 (*Z*) < 0.906 (*E*)] and refractive index [1.543(*Z*) < 1.551 (*E*)].

Thus, to predict the sequence of chromatographic elution of isomers can be used not only reference data on their boiling points, but also (in the absence of such data, for example, for high boiling compounds), the relative densities and refractive indices. The isomers characterized by the lowest values, compared to the others, not only of boiling point, but also of density, and/or refractive index, have minimum retention parameters. All data in Table 1 are consistent with this statement.

This conclusion deserves further comment. If it is of general nature, it is expedient to confirm this by the examples of not only of the (*E*)- and (*Z*)-isomers, but at least of some structural isomers. Table 4 contains the basic physicochemical properties, chromatographic RI, and molar volumes of the four groups of isomeric alkanes $C_nH_{2n+2}$. The described dependence is clearly seen also in this case: In all the isomers with lower $T_b$ the values of densities and refractive indices are also smaller, which corresponds to an increase in the molar volumes by 1.6–2.6 $cm^3$ $mol^{-1}$, but their the molar refractions remain therewith constant up to ±0.1. Thus, to predict the order of chromatographic elution of any isomer not just the boiling temperature, but also such properties as $d_4^{20}$ and $n_D^{20}$ may be used.

Given the above, we can come back to the existence of two groups of (*Z*)- and (*E*)-isomers (two parts of Table 1), namely $T_b(Z)$ and RI (*Z*) > $T_b(E)$ and RI(*E*) ("normal" sequence of boiling points and the relative retention indices), and $T_b(Z)$ and RI(*Z*) < $T_b(E)$ and RI(*E*) ("reverse" order). It is easy to see that these two fundamentally different cases do not directly

**Table 4.** Physicochemical parameters of some isomeric alkanes

| Isoalkane (molecular weight) | $T_b$, °C | $d_4^{20}$ | $n_D^{20}$ | RI | $V_M = M/d_4^{20}$, cm$^3$ mol$^{-1}$ | $MR_D$, cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| *n*-Pentane (72) | 36.1 | 0.626 | 1.357 | 500 | 115.2 | 25.2 |
| 2-Methylbutane (72) | 27.9 | 0.620 | 1.354 | 474±2 | 116.3 | 25.2 |
| 2,2-Dimethylpropane (72) | 9.5 | 0.612 | 1.349 | 412±2 | 117.8 | 25.2 |
| *n*-Hexane (86) | 68.7 | 0.659 | 1.375 | 600 | 130.8 | 29.9 |
| 2-Methylpentane (86) | 60.3 | 0.653 | 1.371 | 570±1 | 132.0 | 29.9 |
| 2,2-Dimethylbutane (86) | 49.7 | 0.649 | 1.369 | 537±2 | 132.8 | 29.9 |
| *n*-Heptane (100) | 98.4 | 0.684 | 1.388 | 700 | 146.5 | 34.5 |
| 2-Methylhexane (100) | 90.1 | 0.679 | 1.385 | 666±2 | 147.6 | 34.5 |
| 2,4-Dimethylpentane (100) | 80.5 | 0.673 | 1.382 | 630±2 | 148.9 | 34.6 |
| *n*-Decane (142) | 174.1 | 0.730 | 1.412 | 1000 | 194.9 | 48.4 |
| 2-Methylnonane (142) | 166.8 | 0.726 | 1.410 | 964±2 | 196.0 | 48.5 |
| 2,7-Dimethyloctane (142) | 160.0 | 0.724 | 1.409 | 929±2 | 196.5 | 48.5 |

depend on the chemical nature of the compounds: nonpolar hydrocarbons, halogenides of medium polarity, and highly polar nitriles exist in both parts of Table 1. Thus, it is presumablethat any attempt to formal-structural (chemometrics, see, for example, [7, 11]) to justify this separation of (*E*)- and (*Z*)-isomers in the two groups is of little promise, which is consistent with their absence to date. However, this problem has a relatively simple solution without the use of molecular parameters and different topochemical descriptors and does not require any complex calculations, and it is consistent with the basic concepts of organic chemistry about the polarity of substituents.

To the first part of Table. 1 ["normal" order of $T_b$ and chromatographic elution, (*Z*) > (*E*)] belong 1,2-disubstituted compounds in which in both positions of the double C=C bonds are either alkyl substituents (in general, the substituents with $sp^3$-hybridized carbon atoms), or of the non-polar substituents capable of conjugation (Y = C=C , C≡C, Ar), or polar functional groups (X = Hal, Ar, OR, CN, etc.) which are arranged symmetrically with respect to the C=C fragment. The second group [the second part of Table 1., "reverse" order of $T_b$ and chromatographic elution of isomers, (*Z*) < (*E*)] consists of the compounds containing double C=C bond with substituents of strongly different polarity [μ(CX) >> μ(CY), where μ is dipole moment of the corresponding bond]. As a result, in the (*E*)-isomers of the first group the two dipole moments of the bond C–C and C–Y are largely compensated (assuming no distortion of the flat structure of the molecules), so that the resultant dipole moment of molecule X(Y)–CH=CH–C(Y) is close to zero, as illustrates the scheme below. In the case of (*Z*)-isomers of the first group the dipole moments of the C–X or C–Y are oriented so that the total dipole moment of the molecule ($\mu_\Sigma$) can be estimated as $\mu_\Sigma \approx 2\mu \cos(\theta/2)$, where θ is the bond angle (θ = 60º). For 1,2-disubstituted unsaturated compounds of the second group, the dipole moments of the C–X, and C–Y groups, on the contrary, contribute additively to the dipole moments of the of (*E*)-isomer resulting in $\mu_\Sigma \approx 2\mu$, whereas in the case of (*Z*)-isomers, they still should be close to the value of $\mu_\Sigma \approx 2\mu \cos 30^\circ$ (see the scheme).

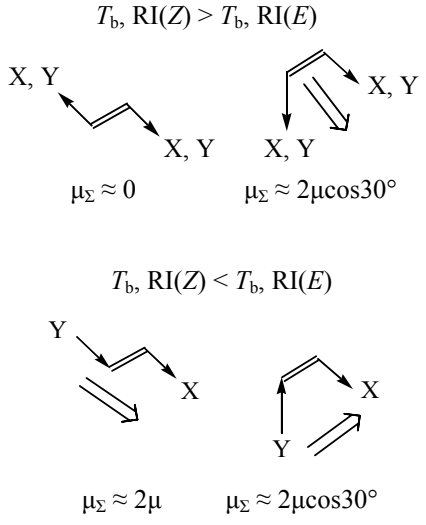


**Table 5.** Dipole moments of some compounds

| Compound | Isomer | μ, D |
|---|---|---|
| 1,2-Dichloroethylene (96) | *E* | 0.70 |
| | *Z* | 1.90 |
| 1-Bromo-2-chloroethylene (140) | *E* | 0 |
| | *Z* | 1.57 |
| 1,2-Dibromoethylene (184) | *E* | 0 |
| | *Z* | 0.75 |
| 1-Iodo-2-chloroethylene (188) | *E* | 0.57 |
| | *Z* | 1.27 |
| Azoxybenzene (198) | *E* | 1.71 |
| | *Z* | 4.68 |
| 1,2-Diiodoethylene (280) | *E* | 0 |
| | *Z* | 0.75 |

**Table 6.** Dipole moments of compounds $CH_3X$

| $CH_3X$ | μ, D | $CH_3X$ | μ, D |
|---|---|---|---|
| $CH_3–CH=CH_2$ | 0.36±0.01 | $CH_3–F$ | 1.83±0.03 |
| $CH_3–C_6H_5$ | 0.36±0.01 | $CH_3–Cl$ | 1.88±0.02 |
| $CH_3–N(CH_3)_2$ | 0.62±0.02 | $CH_3–CO_2CH_3$ | 1.7±0.1 |
| $CH_3–C^{o}CH$ | 0.78±0.01 | $CH_3–CO_2C_2H_5$ | 1.9±0.1 |
| $CH_3–OCH_3$ | 1.3±0.1 | $CH_3–CHO$ | 2.7±0.1 |
| $CH_3–I$ | 1.61±0.02 | $CH_3–COCH_3$ | 2.8±0.1 |
| $CH_3–OH$ | 1.68±0.04 | $CH_3–NO_2$ | 3.4±0.2 |
| $CH_3–Br$ | 1.80±0.02 | $CH_3–CN$ | 3.7±0.2 |

Larger dipole moments of isomers while the dispersion components of intermolecular interactions are approximately equal correspond to larger contributions of dipole-dipole component, which is manifested in the larger boiling points and chromatographic retention parameters.

This conclusion can be confirmed by comparing the reference values of the dipole moments of the various (*Z*)- and (*E*)-isomers containing two polar substituents at the double bond (listed by the increase in their molar masses, see Table 5).

Thus, the existence of two groups of (*Z*)- and (*E*)-isomers of unsaturated compounds (Table 1) can be attributedto the differences in their dipole moments. Such an explanation despite its simplicity has a fairly good predictive capability. For example, dichloroalkenes with a fragment of the structure Cl–C=C–Cl correspond to the "normal" patterns of variation of properties of (*E*) and (*Z*)-isomers, while unsymmetrically substituted monochloroalkenes or nitrites with C=C–Cl or C=C–CN fragments quite naturaly belong to the "reverse" group, etc. Thus, to predict the sequence of chromatographic elution of (*E*)- and (*Z*)-isomers, alongside applying the values of their physicochemical parameters, it is possible to use common knowledge about the polarity of different substituents in the molecules of organic compounds.

If necessary, it is possible as a first approximation for the dipole moments of various functionally substituted alkenes to use the values of the dipole moments of compounds $CH_3X$ arranged in ascending sequence of μ values (see Table 6).

The above suggests a conclusion on the possibility of other ways to estimateRI of (*E*)- and (*Z*)-isomers. If the electron-withdrawing properties of the substituents at the double bond C=C affect the order of chromatographic elution, it severely limits the possibility of additive schemes. The only exception is the recently proposed version, based on the selection of the most appropriate precursors best matching the structure of the considered compound [12, 13].

It may be suggested that the rules proposed above for the simplest 1,2-disubstituted unsaturated compounds are applicable for the compounds with tri- and tetra-substituted C=C bonds. The examples listed in Table 7 confirm the existence of two groups differing by the ratio of their $T_b$ and RI and one-to-one relation between the $T_b$ and RI, although estimates of the total electronic effects in the molecules bearing three or four substituents may not be as unambiguous as in the simple 1,2-disubstituted alkenes.

Some (relatively few) isomeric compounds, whose properties of (*Z*) and (*E*) isomers do not meet the above discussed pattern are worth mentioning. Some examples of these anomalies are shown in Table. 8.

So, $T_b$ of (*Z*)-3-methyl-2-pentene is less than that of (*E*)-isomer, which is consistent with the values of RI, but contradicts the ratios of densities [0.699 (*Z*) > 0.694 (*E*)] and refractive indices [1.404 (*Z*) > 1.402 (*E*)] of these isomers. As noted above, there is always some probability of incorrect assignment of structures of isomers to the values of their physicochemical properties and chromatographic retention parameters. To reveal the causes of each of these abnormalities is difficult, usually it requires the isolation of the isomers

**Table 7.** Physicochemical parameters and chromatographic retention indices of (*E*)- and (*Z*)-isomers of some tri- and tetra-substituted unsaturated compounds

| Compound (molecular weight) | Isomer | $T_b$, °C | $d_4^{20}$ | $n_D^{20}$ | RI |
|---|---|---|---|---|---|
| I. $T_b$, RI (*Z*) > $T_b$, RI (*E*) | | | | | |
| 3-Methyl-2-hexene (98) | *E* | 95.2 | 0.712 | 1.408 | 698±5 |
| | *Z* | 97.3 | – | – | 706±3 |
| 4-Methyl-3-ethyl-2-pentene (112) | *E* | 114.3 | 0.735 | 1.421 | 756±4 |
| | *Z* | 116 | 0.739 | 1.424 | 764±2 |
| 5,5-Dimethyl-2-hexene (112) | *E* | 104.1 | 0.707 | 1.406 | 708±6 |
| | *Z* | 106.9 | 0.717 | 1.411 | 722±5 |
| 2,3-Dichloro-2-butene (124) | *E* | 101.3 | 1.142 | 1.458 | 727±9 |
| | *Z* | 125–126 | 1.162 | 1.459 | 808±13 |
| II. $T_b$, RI (*Z*) < $T_b$, RI (*E*) | | | | | |
| 2-Methyl-2-butenoic nitrile (81) | *E* | 138.2 | 0.831 | 1.432 | 723 |
| | *Z* | 123 | 0.823 | 1.424 | 677±8 |
| 2-Bromo-2-butene (134) | *E* | 87–88 | 1.320 | 1.459 | 666 |
| | *Z* | 83–84 | – | – | – |

**Table 8.** Some anomalies in the general pattern of the ratio of boiling points and chromatographic elution sequences of (*E*)- and (*Z*)-isomers of unsaturated compounds[a]

| Compound (molecular weight) | Isomer | $T_b$, °C | $d_4^{20}$ | $n_D^{20}$ | RI |
|---|---|---|---|---|---|
| I. Exclusions from the rule $T_b$, RI (*Z*) > $T_b$, RI (*E*) | | | | | |
| 3-Methyl-2-pentene (84) | *E* | 70.4 | **0.694** | **1.402** | 618±4 |
| | *Z* | 67.7 | **0.699** | **1.404** | 609±4 |
| 2,2-Dimethyl-3-hexene (112) | *E* | 105.4 | – | – | 718±7 |
| | *Z* | 100.9 | – | – | 699±13 |
| 1,4-Dichloro-2-butene (124) | *E* | 155.5 | – | – | 901±12 |
| | *Z* | 152.5 | – | – | 878±12 |
| Dimethyl 2-butenedioate (144) | *E* | 193.2 | – | 1.406 | **993±2** |
| | *Z* | 205 | – | 1.455 | **982±4** |
| Diethyl 2-butenedioate (172) | *E* | 218 | 1.051 | 1.441 | **1163±3** |
| | *Z* | 222.6 | 1.062 | 1.441 | **1140±3** |
| Pentadec-7-ene (210) | *E* | 267.4 | – | – | 1473 |
| | *Z* | 266.1 | – | – | 1464 |
| II. Exclusions from the rule $T_b$, RI (*Z*) < $T_b$, RI (*E*) | | | | | |
| 2-Chloro-2-butene (90) | *E* | 62.8 | 0.914 | 1.419 | 589±5 |
| | *Z* | 70.6 | 0.924 | 1.424 | 617±4 |

[a] In bold are shown the discrepancies in the values of physicochemical properties and retention indices.

**Table 9.** Physicochemical properties and chromatographic retention indices of some *cis*-and *trans*-isomers of 1,2-disubstituted cyclic compounds

| Compound (molecular weight) | Isomer | $T_b$, °C | $d_4^{20}$ | $n_D^{20}$ | RI |
|---|---|---|---|---|---|
| I. $T_b$, RI (*cis*) > $T_b$, RI (*trans*) | | | | | |
| 1,2-Dimethylcyclopropane (70) | *trans* | 28.2 | 0.670 | 1.374 | 490±9 |
| | *cis* | 37.0 | 0.694 | 1.380 | 515±4 |
| 2,3-Dimethylaziridine (71) | *trans* | 74.5 | 0.785 | 1.407 | 648±16 |
| | *cis* | 82 | 0.800 | 1.412 | 658±14 |
| 2,3-Dimethyloxirane (72) | *trans* | 54.0 | 0.804 | 1.374 | 550±7 |
| | *cis* | 60.0 | 0.828 | 1.383 | 574±11 |
| 2,3-Dimethylthiirane (88) | *trans* | 88–89 | 0.886 | 1.459 | 688±22 |
| | *cis* | 101.8 | 0.928 | 1.475 | 718±2 |
| 1,2-Dimethylcyclopentane (98) | *trans* | 91.9 | 0.751 | 1.411 | 689±5 |
| | *cis* | 99.5 | 0.773 | 1.421 | 724±6 |
| 1,2-Diethylcyclopropane (98) | *trans* | 86.5 | – | – | – |
| | *cis* | 93.5 | – | – | – |
| 1-Methyl-2-propylcyclopropane (98) | *trans* | 88.9 | – | – | – |
| | *cis* | 96.6 | – | – | – |
| 1,2-Dimethyl-3-chlorocyclopropane (104) | *trans* | 91.3 | – | – | – |
| | *cis* | 100–102 | – | – | – |
| 1,2-Dimethylcyclohexane (112) | *trans* | 124.4 | 0.785 | 1.426 | 800±7 |
| | *cis* | 129.7 | 0.794 | 1.435 | 828±6 |
| 1-Methyl-2-ethylcyclopentane (112) | *trans* | 121.2 | – | – | 790±6 |
| | *cis* | 128 | 0.785 | 1.427 | 823±6 |
| 1-Methyl-2-propylcyclobutane (112) | *trans* | 116.2 | 0.737 | 1.409 | – |
| | *cis* | 118.6 | 0.745 | 1.413 | – |
| 1,2-Dichlorocyclohexane (152) | *trans* | 193–194 | 1.184 | 1.490 | 1037±3 |
| | *cis* | 206.9 | 1.202 | 1.495 | 1092±2 |
| II. $T_b$, RI (*cis*) < $T_b$, RI (*trans*) | | | | | |
| 2,3-Dimethyloxirane-2-carbonitrile (97) | *trans* | 155 | 0.960 | 1.412 | – |
| | *cis* | 142–143 | 0.950 | 1.406 | – |
| 2-Methyl-3-ethyloxirane-2-carbonitrile (111) | *trans* | 163–164 | – | – | – |
| | *cis* | 156 | – | – | – |

in pure form, and re-defining their characteristics, which is often extremely difficult. Isomers of a compound like 2,2-dimethyl-3-hexene does not correspond to the general rule of $T_b(Z) > T_b(E)$, although its structural isomer 5,5-dimethyl-2-hexene is consistent with it. In this case, the cause may be the presence of *tert*-butyl group in the α-position to the C=C double bond. Anomalous relation between the properties of 1,4-dichloro-2-butene (*Z*)- and (*E*)-isomers can be associated with a state of the conformational equilibrium in which the dipole moments of the two C–Cl bonds are mutually compensated.

The most "mysterious" example in Table 4 is that of the ethers of (*E*)- and (*Z*)-2-butenedioic acids. The values of $T_b$, $d_4^{20}$ and $n_D^{20}$ of (*Z*)-isomer (maleate) regularly higher than those of (*E*)-isomers (fumarate), which should uniquely identify the sequence of chromatographic elution. However, the order of the retention indices is reversed, i.e., RI(*Z*) < RI(*E*), which is inconsistent with the physicochemical data. Analysis of this discrepancy showed that the retention indices of such esters, including dimethyl fumarate (993, 994) [14, 15], dimethyl maleate (978, 979, 981, 984) [14], diethyl fumarate (1160) [16], and diethyl maleate (1081) [17, 18] were identified in a few papers as early

**Table 10.** Boiling points and retention indices of disubstituted arenes

| Substituents | Isomer | $T_b$, °C | RI | Substituents | Isomer | $T_b$, °C | RI |
|---|---|---|---|---|---|---|---|
| Dimethyl- | *ortho* | 144.4 | 885±9 | Methyl-bromo- | *ortho* | 181.7 | 1018±11 |
| | *meta* | 139.1 | 865±8 | | *meta* | 183.7 | 1020±11 |
| | *para* | 138.4 | 863±8 | | *para* | 184.5 | 1029±10 |
| Dibromo- | *ortho* | 224–225 | 1212±11 | Methyl-chloro- | *ortho* | 159.1 | 934±12 |
| | *meta* | 218 | 1187±11 | | *meta* | 161.9 | 938±12 |
| | *para* | 220.4 | 1162±15 | | *para* | 161.5 | 941±8 |

as in 1980s. It can be assumed that in these cases the elution order of isomers was determined incorrectly, but the RI values were identified correctly. As a result, in the chromatographic identification of the same isomers by other authors these errors were repeated. The other reason for this anomaly, as in the case of 1,4-dichloro-2-butene, can be a position of the conformational equilibrium in which the dipole moments of the two alkoxycarbonyl groups are not antiparallel.

It should be noted in conclusion that all identified patterns relating the chromatographic retention parameters of (*Z*)- and (*E*)-isomers of unsaturated compounds with their physicochemical properties are applicable to the *cis*- and *trans*-isomers of 1,2-disubstituted cyclic compounds (Table 9). The isomers of this type also fall in two groups by the $T_b$/RI ratio, in each of which the compounds with the large boiling point, relative density, and refractive index are characterized by higher retention indices. For these isomers also did not yet existed acceptable ways to estimate RI, or at least, to predict the chromatographic elution sequences. Moreover, the discussed relations make it understandable why the *ortho*-isomers of dialkyl- and dihalo-substituted arenes have maximum $T_b$ and RI values compared with the *meta*- or *para*-isomers, while these parameters are minimal for *ortho*-isomers of monoalkyl-monohalo-sustituted arenes. The cause in this case also should be the electronic effects of the substituents (Table 10).

## EXPERIMENTAL

The values of physicochemical characteristics of (*Z*)- and (*E*)-isomers of unsaturated compounds are taken from the Beilstein Handbook and derived reference editions [19–21]. The source of gas chromatographic retention indices on standard non-polar polydimethylsiloxane stationary phases was the database [6] and the author's own database. All RI values were averaged with the calculation of mean values of standard deviations. The values of dipole moments are calculated by averaging the data from the reference books [21, 22], original publications [23–25], and some online sources [26–29]. Statistical analyzes were performed using the software Origin (version 4.1).

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