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Abstract

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ON THE LIMITED APPLICABILITY OF THE AUWERS–SKITA RULE TO STEREOISOMERIC DIALKYLCYCLANES

In recent years it has been noted more than once that the Auwers–Skita rule, according to which the trans forms of dialkylcyclanes have lower boiling points, refractive indices, and specific gravities, and higher molecular refractions than the cis forms, is not applicable to 1,3-dialkylcyclopentanes and 1,3-dialkylcyclohexanes, since in these series the relation of the properties of the cis and trans isomers is reversed. In the case of stereoisomeric 1,3-dimethylcyclopentanes and 1,3-dimethylcyclohexanes this was confirmed by thermodynamic data and by synthesis.

Recently we observed a case in which, even in the series of 1,4-dialkylcyclohexanes, where the applicability of the Auwers–Skita rule had until now not been disputed by anyone, a peculiar deviation from this rule occurs ([1]). It turned out that in the case of stereoisomeric 1,4-diisopropylcyclohexanes the specific gravity and refractive index are higher, while the molecular refraction and melting point are lower* for the lower-boiling isomer, which, as spectroscopic data showed, is the cis form. Thus, in the case under consideration, contrary to the Auwers–Skita rule, the lower-boiling isomer proved to be not the trans form but the cis form.

In the present work it is shown that the facts accumulated up to now make it possible to approach in a new way the question of the relation between configuration and physical constants, and that the applicability of the Auwers–Skita rule is apparently limited not only by the position of the side chains in the dialkylcyclane molecule, but also by the number of carbon atoms in the latter.

We have already noted ([2]) that in the series of 1,4-dialkylcyclohexanes the boiling points, refractive indices, and specific gravities in each pair of stereoisomers converge with increasing molecular weight of the hydrocarbons. This convergence of constants is the result of their more rapid increase in the trans form than in the cis form as the molecular weight of the dialkylcyclane increases. Such a more rapid increase of the constants naturally opens the possibility that, at a certain molecular weight of the hydrocarbon, one of the constants of the trans forms—for example, the boiling point, usually lower—may become even higher than the corresponding constant of the cis form. This is especially easy to verify if one considers not the boiling points themselves, but their differences for each pair of stereoisomers. Thus, if on a graph one plots the values

$$\Delta t = t_c - t_t,$$

where t_c and t_t are the boiling points of the cis and trans forms at 760 mm, respectively, against the number of carbon atoms in the molecule, it will be seen that the differences obtained lie on a straight line (see Table 1 and Fig. 1, line B). Near C_{11} this straight line intersects the abscissa axis, and consequently the cis forms of 1,4-dialkylcyclohexanes with a number of carbon atoms exceeding 11 must already boil lower than the trans forms. Po-

* In the series of 1,4-disubstituted cyclohexanes, the higher melting point is characteristic of the trans forms.

Table 1

Properties of cis- and trans-isomers of 1,4-dialkylcyclohexanes

Hydrocarbon	b.p., °C/760 mm cis-	b.p., °C/760 mm trans-	b.p., °C/760 mm difference	n_D^{20} cis-	n_D^{20} trans-	n_D^{20} difference	d_4^{20} cis-	d_4^{20} trans-	d_4^{20} difference
1,4-Dimethylcyclohexane (3)	124.321	119.351	4.970	1.42966	1.42090	0.00876	0.78285	0.76255	0.02030
1-Methyl-4-ethylcyclohexane (2)	152.6	149.1	3.5	1.4374	1.4304	0.0070	0.7969	0.7798	0.0171
1-Methyl-4-isopropylcyclohexane (4)	172.7	170.5	2.2	–	–	–	–	–	–
1,4-Diisopropylcyclohexane (1)	215.1*	217.1*	−2.0	1.4524	1.4485	0.0039	0.8236	0.8143	0.0093

* The boiling point was determined in vacuum; here the value is given as found by recalculation according to Dreisbach' s tables (5).

Figure 1. Dependence of the differences in boiling points of stereoisomers on the number of carbon atoms in the molecule. A —1,2-dialkylcyclopentanes; B —1,2-dialkylcyclohexanes; V —1,4-dialkylcyclohexanes

Figure 1: Figure 1. Dependence of the differences in boiling points of stereoisomers on the number of carbon atoms in the molecule. A —1,2-dialkylcyclopentanes; B —1,2-dialkylcyclohexanes; V —1,4-dialkylcyclohexanes

Apparently, it is precisely such a phenomenon that we have encountered in the case of stereoisomeric 1,4-diisopropylcyclohexanes.

Thus, the deviation in the mutual relations of the boiling points of stereoisomeric 1,4-diisopropylcyclohexanes from the Auwers–Skita rule appears to us to be a regular phenomenon. On the other hand, the values of the refractive indices and specific gravities remain, in the case of this hydrocarbon, higher for the cis-form. Evidently, here the lines expressing the dependence of the corresponding differences of constants (Δn and Δd) on the abscissa axis have not yet intersected. It should be noted, incidentally, that at present no definite conclusion can yet be drawn about the geometric form of the dependences of Δn and Δd on the number of carbon atoms in the molecule, because of the insufficiency of experimental data. Nevertheless, the available information shows that in stereoisomeric 1,4-dialkylcyclohexanes these constants also converge with increasing molecular weight (Table 1).

Fig. 1. Dependence of the differences in boiling points of stereoisomers on the number of carbon atoms in the molecule. **A** —1,2-dialkylcyclopentanes, **B** —1,2-dialkylcyclohexanes, **V** —1,4-dialkylcyclohexanes.

The considerations given above make it possible to conclude that stereoisomeric 1,4-dialkylcyclohexanes with 12 or a somewhat larger number of carbon atoms in the molecule should deviate from the rule under consideration analogously to 1,4-diisopropylcyclohexane: the lower-boiling stereoisomers will be cis-forms, which probably should have higher n_D^{20} and d_4^{20}. At still greater molecular weight, the existence of trans-isomers with higher refractive indices and specific gravities than those of the cis-forms is not excluded. Thus, it may be thought that the applicability of the Auwers–Skita rule in the series of 1,4-dialkylcyclohexanes is limited only to the first members of the series.

The fact that the stereoisomers with side chains of different types (methyl, ethyl, isopropyl) satisfy a linear dependence between the differences in boiling points and the number of carbon atoms in the molecule is very remarkable. It apparently means that, for isomeric cyclanes of one series with different radicals, the values of Δt at a given number of carbon atoms in the molecule should be close.

Consideration of the literature data and of our own data on the boiling points of stereoisomeric dialkylcyclanes shows that the line—

···linear character of the relationship between the differences in boiling temperatures of the stereoisomers and the number of carbon atoms in the molecule is not limited only to the series of 1,4-dimethylcyclohexanes. Indeed, from Table 2 and line A in Fig. 1 it is evident that the differences in boiling temperatures of the stereoisomers in the series of 1,2-dialkylcyclopentanes also fall well on a straight line. In the case of 1,2-dialkylcyclohexanes (Table 3 and Fig. 1, line B), the first member of the series, namely 1,2-dimethylcyclohexane, falls out of the linear relationship, whereas the remaining known members of the series satisfy it quite well. However, in the case of these two series the slopes of the straight lines turn out to be considerably less steep than in the case of 1,4-dialkylcyclohexanes, and therefore here an intersection with the abscissa axis, if it occurs, may be expected only for hydrocarbons having 18 and 22 carbon atoms, respectively. Thus, for the stereoisomeric 1,2-dialkylcyclanes considered, the boiling temperatures of the trans forms also increase more rapidly with increasing molecular weight than those of the cis forms, but nevertheless in these cases the Auwers–Skita rule should have a somewhat broader applicability than for 1,4-dialkylcyclohexanes.

Table 2

Properties of cis- and trans-isomers of 1,2-dialkylcyclopentanes

Hydrocarbon	b.p. °C/760 mm cis-	b.p. °C/760 mm trans-	b.p. °C/760 mm difference	n_D^{20} cis-	n_D^{20} trans-	n_D^{20} difference	d_4^{20} cis-	d_4^{20} trans-	d_4^{20} difference
1,2-Dimethylcyclopentane ([8])	99.532	91.869	7.663	1.42217	1.41200	0.01017	0.77262	0.75144	0.02118
1-Methyl-2-ethylcyclopentane ([8])	128.050	121.2	6.8	1.42933	1.4219	0.0074	0.78522	0.7690	0.0162
1-Methyl-2-*n*-propylcyclopentane ([6])	152.58	146.37	6.21	1.43442*	1.42750*	0.0069	0.7921	0.7774	0.0147
1-Methyl-2-*n*-butylcyclopentane ([7])	174.5	169.0	5.5	1.4381	1.4321	0.0060	0.7980	0.7847	0.0133

* For the yellow He line.

Table 3

Properties of cis- and trans-isomers of 1,2-dimethylcyclohexanes

Hydrocarbon	b.p. °C/760 mm cis-	b.p. °C/760 mm trans-	b.p. °C/760 mm difference	n_D^{20} cis-	n_D^{20} trans-	n_D^{20} difference	d_4^{20} cis-	d_4^{20} trans-	d_4^{20} difference
1,2-Dimethylcyclohexane ([8])	129.728	123.419	6.309	1.43596	1.42695	0.00901	0.79627	0.77601	0.02026
1-Methyl-2-ethylcyclohexane ([8])*	155.97	151.69	4.28	1.4432	1.4382	0.0050	0.8094	0.7972	0.0122
1-Methyl-2-*n*-propylcyclohexane ([9])	175.9**	172.1**	3.8	1.4460	1.4408	0.0052	0.8127	0.7997	0.0130
1-Methyl-2-*n*-hexylcyclohexane ([9])	242.6**	239.4**	3.2	1.4527	1.4490	0.0037	0.8208	0.8116	0.0092
1-Methyl-2-*n*-heptylcyclohexane ([9])	260.5**	258.1**	2.4	1.4540	1.4503	0.0027	0.8229	0.8143	0.0086

* Almost simultaneously with the authors of work ([8]), we also synthesized and separated into stereoisomers 1-methyl-2-ethylcyclohexane. The constants we obtained (cis: b.p. 156.05°/760 mm, n_D^{20} 2.4432, d_4^{20} 0.8106; trans: b.p. 151.75°/760 mm, n_D^{20} 1.4383, d_4^{20} 0.7970) practically do not differ from those given in the table, with the exception of the specific gravity of the cis form.

** The boiling temperature was determined in vacuum; the value given here was found by recalculation according to Dreisbach' s tables ([5]).

It should be noted that in the literature there are data for stereoisomeric 1-

methyl-4-*tert*-butylcyclohexanes ([10]), for which the difference in boiling temperatures is 2° (or −2°, since the geometrical configura-

tion of the stereoisomers has not been established), instead of the value close to zero expected for C_{11}. It is possible that this exception from the linear dependence is connected with the large volume of the tert-butyl group.

In conclusion it is necessary to emphasize that, until additional data appear, it remains possible that in all the cases considered the dependence between Δt and molecular weight is expressed not by straight lines, but by curves with a considerable radius of curvature, for example by linear branches of a hyperbola. Indeed, it would be difficult to allow that the differences between the boiling temperatures of stereoisomers can increase to arbitrarily large values. It is more likely to suppose that, beginning with some number of carbon atoms in the molecule, the values of Δt should change more slowly than is required by a linear dependence, or even cease to change altogether. However, this reservation in no way affects the main conclusion of the present work concerning the conditional and limited applicability of the Auwers–Skita rule.

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Note: Figure translations are in progress. See original paper for figures.