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## Abstract

## Full Text

## CHEMISTRY

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# OPTICAL STUDY OF THE CONFORMATIONS OF cis- AND trans-2-METHYL-1-ETHYLCYCLOHEXANOLS

**1.** Investigations of the last 10-15 years have shown ($^{1-6}$) that cyclohexane exists predominantly in the chair form, in which it has a minimum of energy. The potential barrier for the transition of the chair form into the boat form is estimated from 5.6 ($^{5}$) to 9–10 kcal/mole ($^{4}$).

Kohlrausch (1936) and Hassel (1943) were the first to note ($^{1}$) that the C—H bonds of the chair form of cyclohexane can be divided into two groups: 1) those parallel to the $OZ$ axis and 2) those forming an angle of $\pm 19.5^\circ$ $(109.5^\circ - 90^\circ)$ with the $OXY$ plane. Bonds of the first group are now customarily called ($^{7}$) axial and denoted by the letter $a$, and those of the second group—equatorial and denoted by the letter $e$. Carbon atoms 1, 3, 5 and 2, 6, 4 lie in two parallel $OXY$ planes with a distance of 0.5 Å between them. In the chair form of cyclohexane, each equatorial hydrogen atom is at a distance of $\sim 2.5$ Å from the two neighboring axial and two equatorial hydrogen atoms (1,2-interaction). At approximately the same distance each axial hydrogen atom is from the hydrogen atoms of the two neighboring equatorial C—H bonds (1,2-interaction) and from two neighboring axial C—H bonds located on the same side of the ring (1,3-interaction). The indicated distance is approximately two van der Waals radii of a hydrogen atom; therefore the repulsive forces between the hydrogen atoms considered are small. This accounts for the energetic preference of the chair form over the boat form, in which the indicated distances ($\sim 1.83$ Å) are smaller than the sum of two van der Waals radii of hydrogen atoms.

All six axial hydrogen atoms of the ring can become equatorial, and vice versa, without breaking carbon–carbon bonds, by inversion*. The potential barrier of inversion transformations in cyclohexane is small. However, already in the case of monosubstituted cyclohexanes the situation changes substantially. Substituents with a larger van der Waals radius than that of a hydrogen atom experience considerable repulsive forces as a result of 1,2- and 1,3-interactions, and an energetic preference for equatorial substitution already appears: $1e$ in monosubstituted, $1e, 2e$ in ortho-disubstituted cyclohexanes, etc. This preference was confirmed experimentally by Hassel ($^{1}$) (electronographically), which enabled him to formulate the rule: the most stable isomer in a series of polysubstituted cyclohexanes is the isomer with the greatest number of equatorial substituents. In connection with the above, we shall mention another general rule (Barton ($^3$)): in a series of polysubstituted cyclohexanes, in the case of different substituents, the most stable is the isomer with the equatorial position of the larger substituent.

2. In the thirties, Chiurdoglu ($^8$) identified the cis and trans isomers of a series of substituted cyclohexanes, including cis- and trans-1,2-dimethylcyclohexanols; however, he did this without distinguishing their conformations. Two of us ($^9$) synthesized cis- and trans-2-methyl-1-ethylcyclohexanols—(I) and (II)*. They were characterized by their physicochemical properties and were also converted into the known pair ($^8$) of cis- and trans-1,2-dimethylcyclohexanols (III) and (IV) according to the scheme:

cis-2-methyl-1-ethylcyclohexanol $\xrightarrow{H_2/Pd/CaCO_3}$ ethynyl alcohol $\xrightarrow{KMnO_4}$ hydroxy acid $\xrightarrow{LiAlH_4}$ hydroxymethyl al

trans-2-methyl-1-ethylcyclohexanol $\xrightarrow{H_2/Pd/CaCO_3}$ ethynyl alcohol $\xrightarrow{KMnO_4}$ hydroxy acid $\xrightarrow{LiAlH_4}$ hydroxymethyl

However, it is chemically impossible to determine the conformations of these compounds precisely. In the present work this question is investigated by the method of combinational light scattering.

The spectra were recorded in the liquid phase on a domestic ISP-51 spectrograph with a medium camera, using the exciting blue line 4358 Å of a mercury lamp.** Cis-2-methyl-1-ethylcyclohexanol, $\Delta\nu$ cm$^{-1}$: 105(0), 122(0), 146(2), 175(1*), 194(0*) 210(0), 284(3), 322(3), 343(2), 379(4 sh dbl), 415(0), 451(4), 471(1), 492(5), 537(2), 572(1), 605(1), 682(7*), 693(4*), 707(2*), 718(0), 740(0), 759(0), 779(2), 802(3), 822(2*), 836(4*), 862(4), 885(3), 905(1), 921(0), 937(4), 984(6*), 992 (2*), 1015(6), 1045(5), 1067(5), 1096(6), 1122 (1 sh), 1153(6*) –1168(6*) band, 1230(1), 1263(6), 1308(2), 1345(3 sh dbl), 1443(9*), 1466 (8*), 2650(1*), 2681(1*), 2713(1**), 2737(1**), 2852(6*), 2866(6*), 2886(3*), 2902(3*), 2915(3*), 2936(10*), 2945(10*), 2957(4*), 2974(4*), 3122(2), 3183 (2 band), 3275–3576, (3 band), 3594(1), 3604(4), 3619(1), 3636(1).

Trans-2-methyl-1-ethylcyclohexanol, $\Delta\nu$ cm$^{-1}$: 84(0), 109(0), 121(0), 185(0), 212(0), 249(1), 280(1), 312(1), 365(0), 400(4) 434(5), 451(6*), 468(4*), 497(4), 525(0), 555(5), 586(4), 610(0), 634(1), 662(0), 683(6*), 693(8*), 705(3*), 807(3), 831(6), 865(5), 890(3), 913(3), 945(3*), 961(7*), 973(7*), 994(5), 1020(6), 1046(5), 1077(3*), 1091(7* sh), 1146(3**), 1171(7 sh**), 1209(3*),

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* Different spatial forms of a molecule that can transform into one another solely by the corresponding rotation of atoms without breaking interatomic bonds are called conformations.

Figure 1. Spectra of the combined light scattering of cis- and
trans-2-methyl-1-ethylcyclohexanols in the region of the hydroxyl group

Figure 1: Figure 1. Spectra of the combined light scattering of cis- and trans-2-methyl-1-ethylcyclohexanols in the region of the hydroxyl group

1223(3*), 1263(7** dbl), 1292(3**), 1305(3**), 1339(5*), 1353(5*), 1445(9**), 1465(8**), 2652(1**), 2679(1**), 2731 (1*), 2772(1*), 2845(6**), 2863(6**), 2873(4**), 2892(4**), 2906(4**), 2927(10**), 2944(10**), 2957(4**), 2976(2*), 3088(3), 3157(3 sh, band), 3350–3574 (4 band), 3581(1), 3604(1*), 3619(4*) 3662(1).

In addition, 10% (by volume) solutions of these substances in carbon tetrachloride were recorded.

3. In examining the optical data obtained, we shall rely on the following experimentally substantiated propositions.

a) As was established by us ([10,11]), the influence of neighboring atoms in a molecule (halogens, oxygen, secondary and tertiary carbon atoms, etc.) on C–H and O–H bonds is opposite***: the former become electronized (their internuclear distance decreases, the bond energy and vibrational frequency increase), whereas O–H bonds become protonized (the internuclear

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* The cis and trans isomers are defined according to the position of the alkyl radicals, which in the present case are the largest substituents.

** Notation for intensities: sh–broad line, r–sharp line, dbl–double line; asterisks denote lines situated on a background common with neighboring lines marked by the same number of asterisks.

*** In the cited works we clarified the factors determining this opposite influence.

**Fig. 1.** Spectra of the combined light scattering of cis- and trans-2-methyl-1-ethylcyclohexanols in the region of the hydroxyl group.

Labels in the figure:

- Isomer (I)
  - Hg 5461 Å
  - OH 3604 (4), 3689 (1) $\mathrm{cm}^{-1}$
  - CH band 3275-3578 $\mathrm{cm}^{-1}$
  - CH
  - Hg 4916 Å
- Isomer (II)
  - Hg 5451 Å
  - OH 3604 (1), 3619 (4) $\mathrm{cm}^{-1}$

- CH band 3350-3578 cm$^{-1}$
- CH
- Hg 4916 Å

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distance, the bond energy decreases, and the vibrational frequencies are lowered):

| | | O—H (cm$^{-1}$) | High-frequency edge of C—H vibrational frequencies (cm$^{-1}$) |
|---|---|---|---|
| Butyl alcohol | primary | 3632 | 2962 |
| ” | secondary | 3622 | 2972 |
| ” | tertiary | 3615 | 2978 |

The directions of the changes in the frequencies of the O—H and C—Cl, O—H and C—O bonds, etc., in the corresponding cases also remain opposite.

b) The influence of a ring on bond frequencies in a ring is known to be especially significant in strained cyclic systems, for example in cyclopropane. In cyclohexane it decreases, but nevertheless remains appreciable. This can be judged, for example, from the high-frequency edge of the vibrational frequencies of the C—H bonds of methylene groups, which in cyclohexane is considerably higher than in normal paraffins: *n*-paraffins —2908, cyclopropane—3080, cyclopentane—2969, cyclohexane—2941 cm$^{-1}$ ([10,12,13]). The ring also affects the C—O, C—D, C—Cl, and other bonds. At present it is generally considered experimentally substantiated (by the method of infrared spectroscopy) that the vibrational frequency of the indicated bonds is higher in their equatorial position than in the axial one ([3,14–18]).

c) In accordance with what was stated in points a) and b), it may be concluded that an equatorial hydroxyl should be more protonated than an axial hydroxyl (i.e., have a lower bond frequency and energy and a larger interatomic distance).

d) The pulsation frequency of trans-ortho-substituted cyclohexanes (as well as cyclopentanes and cyclobutanes) is, as a rule, higher than that of the corresponding cis-ortho-substituted compounds ([12,13]). According to what was set forth above, these data for the trans isomers refer to ee conformations, and the data for the cis isomers to ep conformations.

4. In the liquid phase, cis- and trans-2-methyl-1-ethylcyclohexanols (I) and (II) form an intermolecular hydrogen bond. A vivid manifestation of it in the spectra is the broadening of the frequency of the hydroxyl group into

a band toward the long-wavelength side of the spectrum, especially pronounced in I, which apparently indicates the more acidic character of this hydroxyl (see Fig. 1 and the spectral frequencies given above). On the high-frequency side of these bands, a broadened line is observed, representing a set of closely spaced frequencies. In the spectra of solutions of these substances the broadened bands disappear, since the intermolecular hydrogen bonds in these solutions are broken; the lines on the high-frequency side of the bands remain; they belong to monomers (in the liquid phase not all molecules of the I and II isomers are included in the hydrogen bond). In the spectrum of isomer I the most intense of these lines is 3604, and in II it is 3619 $\text{cm}^{-1}$. The presence of each of the two mentioned frequencies with weakened intensity in the spectrum of the other isomer indicates either a small impurity of the epimer or the state of a certain mobile equilibrium in which these epimers are found. The other frequencies adjoining these lines represent either traces of rotational-vibrational spectra (see below), or else traces of other conformations present in small quantity in the mixture. Since the O—H frequencies, in contrast to the frequencies of the C—O, C—Cl, C—D, and other bonds, must be higher for axial hydroxyls than for equatorial ones (see above), in isomer I with a hydroxyl-group frequency of 3604 $\text{cm}^{-1}$ the C—OH bond is equatorial, while in isomer II with a hydroxyl-group frequency of 3619 $\text{cm}^{-1}$ it is axial.

5. The pulsation frequency in the spectra of epimers I and II, both in their liquid state and in solutions, is also not single, but tripled. The most intense frequency for isomer I is 682 $\text{cm}^{-1}$, and for isomer II 693 $\text{cm}^{-1}$. According to the data given above, the second frequency refers to the trans isomer, the first to the cis isomer. In the spectra of solutions these frequencies are retained.

Each of them, with weakened intensity, is found in the spectrum of the other substance—analogously to the corresponding frequencies of the hydroxyl group for the same reasons (see above). The presence in the spectra of both isomers of a weak frequency of 705 $\text{cm}^{-1}$ indicates a probable admixture, in insignificant amounts, of other conformations.

*(Structural diagrams labeled "ep" and "ee" ; (A).)*

Since in I, which is the cis isomer, as we have seen, the C—OH bond is equatorial, whereas in II, the trans isomer, it is axial, it follows that the first isomer is the ep epimer, the second the ee epimer (more precisely, these are their predominant conformations; apparently there are also admixtures of others).

6. This is also confirmed (in agreement with what was said above in item 6) by the data on the frequencies of the C—O bonds: in the spectrum of isomer I the system of frequencies in the region belonging to vibrations of the C—O bond is shifted to the short-wavelength side relative to the spectrum of isomer II:

II 961(7*), 973(7*), 994(5), 1020(6), 1046(5)
I 984(6), 1015(6), 1045(5), 1067(5)

7. In isomers I and II the constituent parts of the molecules (ethyl and methyl radicals, hydroxyl) possess freedom of rotation about single bonds; in the complex formed by a hydrogen bond, its parts can rotate about the C—O bonds (within the complexes). This rotational (free or restricted) motion of individual parts of the molecule and of the complex is apparently the source of conformational transformations in the compounds considered and of the appearance in the mixture, in addition to the principal conformations found, of small amounts of others, including unstable boat-shaped ones with a pulsation frequency apparently above 802 cm$^{-1}$ (19).

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