M. I. BATUEV, A. A. AKHREM, A. D. MATVEEVA, A. V. KAMERNITSKII

and Academician **I. N. NAZAROV

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Reaction scheme showing conversion of ortho-methylcyclohexanone to cis- and trans-2-methyl-1-ethynylcyclohexanols (I), (II), and, in 5 stages, to cis- and trans-1,2-dimethylcyclohexanols (III), (IV), as well as formation from ortho-methylcyclohexanone with CH_3MgJ.

Figure 1: Reaction scheme showing conversion of ortho-methylcyclohexanone to cis- and trans-2-methyl-1-ethynylcyclohexanols (I), (II), and, in 5 stages, to cis- and trans-1,2-dimethylcyclohexanols (III), (IV), as well as formation from ortho-methylcyclohexanone with CH_3MgJ.

Abstract

Full Text

M. I. BATUEV, A. A. AKHREM, A. D. MATVEEVA, A. V. KAMERNITSKII

and Academician **I. N. NAZAROV**

OPTICAL STUDY OF THE CONFORMATIONS OF CERTAIN GEM-SUBSTITUTED CYCLOHEXANES

The physical properties and reactivity of a functional group depend on its position in the conformation*—axial or equatorial. This position can sometimes be established chemically, but often this is possible only by physical methods of investigation ([1,2]).

In the present work we attempt to determine optically the conformations of the epimeric 2-methyl-1-ethynylcyclohexanols (I), (II), and 1,2-dimethylcyclohexanols (III), (IV), which we synthesized earlier ([3]). The liquid mixture of acetylenic alcohols (I) and (II), obtained from ortho-methylcyclohexanone by the Favorskii reaction, was separated into isomers by prolonged freezing-out of the crystalline cis-isomer (I), followed by its crystallization. The liquid trans-isomer (II) then contained up to 10% admixture of isomer (I). The mixture of alcohols (III) and (IV), obtained by reaction of ortho-methylcyclohexanone with methylmagnesium iodide, was separated by distillation on a column with an efficiency of 40 theoretical plates. The constants of the resulting cis- and trans-isomers (III) and (IV) coincided with the literature values ([4]). Chiurdoglu was the first to identify the cis- and trans-forms of 1,2-dimethylcyclohexanol (III) and (IV), on the basis of Auwers–Skita' s rule, the rule of trans-elimination of water, and the rule of hydrogenolysis that he discovered ([4]). However, the conformation of these compounds was not established by him. The acetylenic alcohols (I) and (II) had previously been converted by us into the known pair of cis- and trans-carbinols (III) and (IV) without affecting the asymmetric center ([3]).

The physical properties of the compounds obtained (I)—(IV) are given in Table 1.

The Raman spectra were recorded in the liquid phase on an ISP-51 spectrograph with the medium camera from the exciting blue line 4358 Å of a mercury lamp**:

(I) 2-Methyl-1-ethynylcyclohexanol-cis, $\Delta\nu$ cm^{-1}: 82 (2), 92 (2), 114 (3*), 124 (3*), 153 (6**) 166 (3**), 179 (3**), 212 (2), 222 (4), 231 (4), 240 (1), 258 (1), 289 (1), 301 (0), 323 (3*), 332 (3*), 358 (1), 373 (1), 387 (1), 402 (3), 442 (2*p), 450 (2*p), 473 (4 dv), 490 (0), 526 (2*), 540 (1*), 593 (3), 624 (1p), 637 (1p), 649 (1*), 661 (8*), 691 (1), 704 (1), 804 (2), 838 (3), 863 (2), 888 (1), 908 (1), 928 (1), 963 (0), 985 (4*), 997 (4*), 1057 (4*), 1067 (4*), 1090 (1), 1114 (4*), 1127 (2*), 1155 (4**), 1166 (4**), 1195 (1), 1212 (2), 1225 (1), 1251 (1), 1266 (4 doublet), 1295(1), 1332 (2*), 1346 (2*), 1358 (2*), 1447 (6**), 1456 (1**), 1467 (3**), 2090 (1), 2101 (6 broad, doublet), 2118 (1), 2851 (6), 2864 (4), 2893 (3*), 2909 (3*), 2922 (4*), 2933 (8*), 2945 (8*), 2957 (2*), 2969 (2*), 2984 (1*), 3269 (1**), 3283 (1**), 3293 (3**), 3315 (1**), 3350—3600 (1, band), 3585 (1), 3600 (3), 3615 (1), 3631 (1), 3654 (1).

(II) 2-Methyl-1-ethynylcyclohexanol-trans, $\Delta\nu$ cm^{-1}: 78 (2*), 92 (2*), 116 (2**), 126 (2**), 152 (5 broad*), 182 (3*), 214 (3**), 227 (3**), 264 (0), 288 (0), 315 (0*), 333 (3*), 338 (0*), 362 (0), 380 (0), 398 (4), 421 (0), 448 (0), 468 (4), 489 (3), 530 (3), 553 (3), 592 (3), 649 (3), 660 (4), 696 (7*), 705 (2*), 806 (3p), 833 (4), 864 (3p), 896 (1), 925 (1), 967 (2*p), 983 (3*p), 996 (4*p), 1033 (1), 1056 (4*), 1064 (4*), 1114 (3**), 1129 (3**), 1153 (4*), 1168 (4*), 1194 (2**), 1213 (2**), 1230 (2**), 1248 (1*), 1263 (4*), 1268 (1*), 1302 (2 doublet), 1329 (3*), 1346 (4* doublet), 1447 (8**), 1459 (4**), 1463 (4**), 2093 (1*), 2105 (9* broad, doublet), 2118 (1*), 2655 (1 broad*), 2684 (1* broad), 2735 (3), 2809 (1), 2854 (6*), 2903 (2*), 2919 (2*), 2930 (10*), 2942 (10*), 2970 (4*), 2983 (2*), 3268 (1**), 3283 (1**), 3298 (1**), 3314 (3**), 3350—3614 (1, band), 3581 (1), 3593 (1), 3614 (3), 3629 (1), 3653 (1).

III) 1,2-Dimethylcyclohexanol-cis, $\Delta\nu$ cm^{-1}: 245 (0), 273 (3*), 291 (3*), 328 (3), 368 (4*), 387 (4*), 444 (4), 484 (1), 524 (6), 566 (3), 603 (3), 622 (1), 695 (10), 803 (3), 835 (5), 857 (5), 888 (4), 915 (4), 939 (4*), 951 (6*), 980 (4p), 988 (6), 1014 (5), 1064 (5), 1092 (5), 1153 (4*), 1170 (6), 1189

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* In the article the conformations are determined from the mutual position of the largest substituents, in this case the methyl and ethynyl groups.

** Designations for intensities: sh —broad line, p —sharp line, dv —double line; asterisks denote lines situated on a background common with neighboring lines; the same number of asterisks denotes lines with the same background. The spectra of isomers (III) and (IV) were published in (5), but in incomplete form, ending according to the frequent part ~ 1450 cm^{-1}.

(1*), 1214 (0), 1237 (3), 1262 (7* broad), 1275 (2*), 1304 (2), 1335 (4*), 1350 (4*), 1369 (0), 1409 (0), 1441 (9*), 1457 (4*), 1471 (2*), 2629 (0), 2659 (0), 2720 (0), 2857 (6*), 2895 (2*), 2914 (4*), 2928 (10*), 2943 (10*), 2970 (4*), 2985 (4*), 3330–3500 (2, band), 3580 (1), 3606 (4), 3619 (1), 3639 (1), 3652 (1).

(IV) 1,2-Dimethylcyclohexanol-trans, $\Delta\nu$ cm^{-1}: 204 (0 broad), 230 (0 broad), 330 (0 broad), 369 (1 broad), 442 (4 doublet), 468 (0 doublet), 497 (3), 519 (0), 536 (0), 556 (5), 580 (0), 617 (0), 658 (0), 673 (0), 698 (10), 765 (0), 798 (3), 829 (4), 857 (5), 888 (3), 909 (3), 944 (6), 969 (0), 988 (3*), 1007 (6*), 1039 (0), 1061 (3), 1088 (5), 1109 (1p), 1122 (1p), 1139 (1p), 1154 (1p), 1175 (6), 1215 (1*), 1234 (3*), 1263 (5**), 1277 (5**), 1303 (2 broad, doublet), 1331 (3*), 1347 (3*), 1358 (3*), 1435 (1*), 1449 (6**), 1465 (3**), 2664 (0), 2728 (0), 2853 (6*), 2871 (5*), 2899 (4*), 2923 (10*), 2936 (10*), 2965 (4*), 2982 (3*), 3380–3530 (2, band), 3582 (1), 3608 (1), 3619 (4), 3636 (1), 3659 (1).

Ten-percent solutions of the first two substances in carbon tetrachloride were also recorded.

In the combination-scattering spectra of each of the two isomers of the acetylenic alcohols studied by us, (I) and (II), and of their solutions in carbon tetrachloride, for the pulsation vibration of the ring and for the vibrations of the $C \equiv C$, $C—H$ in $-C \equiv C—H$, and $O—H$ bonds (in the monomers), not one characteristic frequency but three or four were found (see Table 2). At the same time, in the spectrum of the cis-isomer I and of its solution in carbon tetrachloride—

Table 1

Physical properties of 2-methyl-1-ethynylcyclohexanols (I), (II) and 1,2-dimethylcyclohexanols (III), (IV)

Compounds	M.p., °C	B.p., °C/mm Hg	n_D^{20}
(I) 2-methyl-1-ethynylcyclohexanol-cis	56–57	75/10	1.4780
(II) 2-methyl-1-ethynylcyclohexanol-trans	(liquid)	69–70/10	1.4770
(III) 1,2-dimethylcyclohexanol-cis	23.5–24	74.5/15.5	1.4665
(IV) 1,2-dimethylcyclohexanol-trans	11.5–13	61/13	1.4639

carbon, for each of the indicated characteristic bonds, one line is distinguished by its greater intensity, which is also present in the spectrum of the trans-isomer II, but with weakened intensity. Conversely, the most intense of these characteristic frequencies in the spectra of the trans-isomer II and of its solution in carbon tetrachloride is present with sharply weakened intensity in the spectra of the cis-isomer I. This indicates the presence of an admixture of the predominant conformation of one isomer in the other (especially I in II, see above). The presence in the spectra of both isomers I and II and of their solutions in carbon tetrachloride, in the region of the mentioned characteristic frequencies, of other weak-intensity lines (see Table 2) indicates the possible presence in the mixture with the predominant conformations, in small amounts, also of other conformations (possibly even with the boat form). To the mixture of conformations in I

Table 2

Frequencies of vibrations of characteristic bonds of cis- and trans-2-methyl-1-ethynylcyclohexanols*

Compound	Frequency of the ring pulsation vibration	C C	C–H in – C CH	O–H (monomer)
(I) 2-methyl-1-ethynylcyclohexanol-cis	649 (1)661 (8)691 (1)704 (1)–	–2090 (1)2101 (6sh, dw)2118 (1)–	3269 (1)3283 (1)3293 (3)3315 (1)–	3585 (1)3600 (3)3615 (1)3631 (1)3654 (1)
10% (I) + CCl_4	648 (1)660 (3)688 (1)703 (1)–	2091 (1)2100 (4)2140 (2)2121 (1)–	3270 (1)3285 (1)3293 (3)3317 (1)–	3585 (1)3603 (3)3615 (1)3634 (1)3654 (1)
(II) 2-methyl-1-ethynylcyclohexanol-trans	649 (3)660 (4)696 (7)705 (1)–	–2093 (1)2105 (9sh, dw)2148 (1)–	3268 (1)3283 (1)3298 (1)3314 (3)–	3581 (1)3593 (1)3614 (3)3629 (1)3653 (1)
10% (II) + CCl_4	651 (1)662 (0)695 (4)706 (2)–	2092 (1)2099 (2)2108 (4)2122 (1)–	3270 (1)3283 (1)3298 (1)3314 (3)–	3580 (1)3599 (1)3614 (1)3630 (3)3651 (1)

* The intensities of the lines of pure substances and of solutions are not comparable with one another, since the spectra of the solutions were recorded with a considerably longer exposure; the relative intensity of the lines within the given spectrum is significant. For the O–H bond, the vibration frequencies are given for hydroxyl groups of molecules apparently not included in complexes associ-

structural formulas of conformations (I) ae and (II) ee

Figure 2: structural formulas of conformations (I) ae and (II) ee

ated through a hydrogen bond; for the O—H bonds of the latter, a broad band shifted toward lower frequencies is characteristic (see the spectra above).

and II indicates a considerably larger number of observed lines in their spectra compared with the theoretically expected number (even without taking possible degeneracy of vibrations into account), if these substances had only one conformation each. Let us turn to determining the predominant conformations in (I) and (II), characterized by the most intense vibration frequencies of the characteristic bonds.

The lower frequency of the ring pulsation vibration, 661 cm^{-1}, in isomer (I) compared with the frequency 696 cm^{-1} in isomer (II) confirms (1) that isomer (I) is indeed the cis form, and isomer (II) the trans form, of 2-methyl-1-ethynylcyclohexanol. The conformations of these compounds can be judged from the other listed vibration frequencies of the characteristic bonds. The intense vibration frequencies of the C C bonds in the liquid cis and trans isomers (I) and (II) proved to be merged; in the spectra of the solutions these frequencies are separated, and in (I) the vibration frequency of the C C bond (2100 cm^{-1}) is lower than in II (2108 cm^{-1}). Similarly, the vibration frequencies of the C—H bond in —C CH (3293 cm^{-1}) and O—H (3600 cm^{-1}) in (I) are lower than in (II) (respectively 3314 and 3614 cm^{-1}). According to (1), this means that the predominant conformation in the cis isomer (I) is *ae*, and in the trans isomer (II), *ee*:

In the *ae* conformation the influence of the ring on the hydroxyl group, which is in the equatorial position, is more significant than in the *ee* conformation, in which it is in the axial position. In the *ae* conformation, the equatorial

the hydroxyl group is more protonated; in this connection it has a lower vibrational frequency (3600 cm^{-1}), a lower bond energy, and a greater interatomic distance, i.e., it has more acidic properties than the axial hydroxyl group in the *ee* conformation. Conversely, the bonds $C \equiv C$, $C - H$ in $-C \equiv CH$ in the equatorial position, in which they are found in the *ee* conformation, are more electronized, i.e., have higher vibrational frequencies, bond energy, and a smaller interatomic distance than in the axial position in the *ae* conformation (1,6).

In the isomers of 1,2-dimethylcyclohexanol the pulsation frequency of the ring (695 cm^{-1}), although only slightly, is nevertheless lower in (III) than in (IV) (698 cm^{-1}). This indicates that (III) is the cis- and (IV) the trans-isomer (1). At the same time, the lower vibrational frequency (3608 cm^{-1}) of the hydroxyl group in (III) (monomer), as compared with its vibrational frequency in (IV) (3618 cm^{-1}), indicates that the hydroxyl group in isomer (III) occupies the equatorial position and that the latter exists in the *ae* conformation. In isomer (IV), on the contrary, the hydroxyl group occupies the axial position and isomer (IV) exists in the *ee* conformation. The presence of other weak-intensity frequencies in the region of the vibrational frequencies of the hydroxyl group of monomeric molecules indicates that in samples (III) and (IV) there is apparently also an admixture of other conformations, but in a very insignificant amount.

The dependence between reactivity and conformation in a series of cyclohexane derivatives was observed by us earlier (^{7}). It was shown that the cis-α-ketol (V), obtained from (I), with the equatorial, more acidic hydroxyl is acetylated under milder conditions than the trans-α-ketol (VI), obtained from (II), with the axial position of the hydroxyl:

$$\text{(I)} \xrightarrow[H_2O]{HgSO_4} \text{(V)} \xrightarrow{CH_3COCl\text{-ether}} \text{acetylated product,}$$

$$\text{(II)} \xrightarrow[H_2O]{HgSO_4} \text{(VI)} \xrightarrow{CH_3COCl\text{-ether}}$$

Institute of Fossil Fuels
Academy of Sciences of the USSR

Institute of Organic Chemistry
Academy of Sciences of the USSR

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* We note in passing misprints in (^{1}). On p. 424: in the scheme after the first line from the top on the left side of the first row of formulas the number I should be placed, on the left side of the second row of formulas the number II; between the first and second formulas, both in the first and in the second row of formulas, the arrows should be reversed to the left; in the scheme on p. 423, instead of the designations (p), (a) should be placed; on p. 426, line 13, and in the scheme, instead of ep, ea should be placed.

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

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