ESTABLISHMENT OF THE CONFIGURATION OF STEREOISOMERIC 1,4-DIALKYLCYCLOHEXANES ACCORDING TO THE VIBRATION SPECTRA

COMMUNICATION 1. 1-n-ALKYL-4-TERT-ALKYLCYCLOHEXANES

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In [1] we generalized data on the characteristic spectral peculiarities of dialkylcyclohexanes, permitting the detection of a stereoisomer possessing an axial alkyl radical. Among the tert-alkylcyclohexanes, we studied the spectra of cis- and trans-isomers of 1-methyl-4-tert-butyl and 1-methyl-4-tert-amylcyclohexanes [2]. In the spectra of their cis-isomers, just as in the spectra of other cis-1,4-derivatives, there are comparatively intense IR bands and Raman lines in the region of 600-650 cm^{-1}. In the spectra of the trans-isomers, these bands and lines are either entirely absent or are very weak. The voluminous tert-alkyl radical in these compounds is situated in an equatorial position, while the axial position in the cis-isomers is occupied by the methyl group.

It seemed interesting to us to investigate analogous compounds with somewhat complicated axial or equatorial alkyls and to refine the observed patterns [2]. For this purpose the spectra of three pairs of stereoisomeric dialkylcyclohexanes synthesized for the first time were taken: 1-methyl-4-(1,1-dimethylpentyl)- (I), 1-ethyl-4-tert-butyl- (II), and 1-ethyl-4-tert-amylcyclohexane (III).

EXPERIMENTAL

For the conditions of production of the spectra, see [3, 4]. The IR absorption spectra in the region of 450-3100 cm^{-1} are cited in Figs. 1 and 2, and the frequencies and intensities of the Raman spectra are given in the text.

All the hydrocarbons studied were synthesized by hydrogenation of the corresponding dialkylbenzenes, while the mixtures of stereoisomers obtained were separated either by precise fractional distillation or by a new thiourea method [5, 6], permitting stereoisomers to be separated even if they form adducts with thiourea. The constants are given for each hydrocarbon, and the boiling points under vacuum are experimental, while the calculated values obtained from the experimental data using the Dreisbach tables [7] are indicated for 760 mm.

Cis-1-methyl-4-(1,1-dimethylpentyl)cyclohexane (Cis-I). Cis-I was produced from p-1,1-dimethylpentyltoluene [8] by hydrogenation on platinized charcoal (20% Pt) in a flow-type system, with a volume velocity of 0.15 h^{-1} in a stream of hydrogen at atmospheric pressure and 130-140°. The reaction proceeded to an extent of only 77%; therefore the cyclohexane hydrocarbon was isolated chromatographically on silica gel, and the aromatic and transitional fractions were rehydrogenated; this operation was repeated twice. The mixture of stereoisomers obtained, free of aromatic hydrocarbons, was subjected by continuous multiday round-the-clock distillation on a column with an efficiency of 100 theoretical plates. The distillation was conducted under vacuum at 13 mm with a reflux ratio of 200; the distillate was collected in portions of several grams; a total of 17 fractions were collected. They were analyzed on a capillary chromatograph, and the fractions with close frequencies were combined. Properties [8]: bp 118.2° (13 mm) and 250.1° (760 mm); n_D^{20} 1.4590; d_4^{20} 0.8347; degree of purity 97.3% (the only impurity is the trans-isomer).

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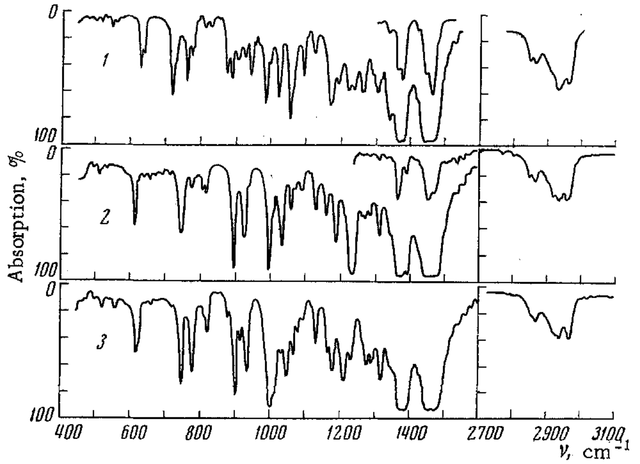

Fig. 1. IR absorption spectra of cis-isomers: 1) 1-methyl-4-(1,1-dimethylpentyl)cyclohexane; 2) 1-ethyl-4-tert-butylcyclohexane; 3) 1-ethyl-4-tert-amylcyclohexane (thickness of the absorbing layer of the substance 0.1 mm).

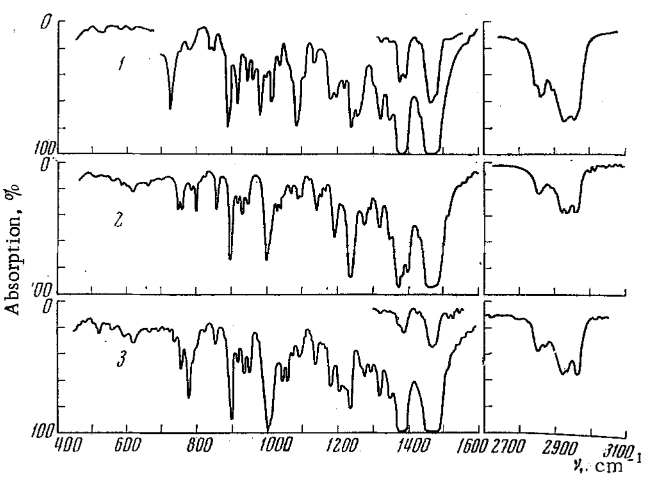

Fig. 2. IR absorption spectra of the trans-isomers (for notations, see Fig. 1).

Raman Spectrum* (Δν, cm^{-1}): 205(5, d, br), 228(4, d, br), 280(8), 288(11), 313(9), 347(5), 374(4), 399(2), 418(1), 443(0), 455(1), 474(4), 501(3), 546(3), 571(1), 625(16, s), 634(12, s), 671(1, br), 710(2), 738(1), 768(62, s), 783(11), 816(6), 833(7), 877(9), 891(10), 911(12), 930(9), 951(11, br), 969(10), 985(2), 1002(1), 1028(19), 1058(32), 1069(22), 1080(2), 1097(15, b), 1128(17, b), 1168(27, b), 1194(22, b), 1224(12, b), 1243(9, b), 1271(25), 1300-1320(18, band), 1340(22), 1363(5), 1382(4), 1441(76), 1467(39), 2851(170, b), 2872(140, b), 2900(290, br, b), 2933(180, d, b), 2961(200, b).

Trans-1-methyl-4-(1,1-dimethylpentyl)cyclohexane (Trans-I). Trans-I was produced together with the preceding compound and separated from it by fractional distillation on a column. Properties [8]: bp 117.1° (13 mm) and 248.7° (760 mm); n_D^{20} 1.4548; d_4^{20} 0.8243; degree of purity 99.0%.

Raman Spectrum (Δν, cm^{-1}): 217(2), 251(9, br), 298(7, br), 332(2), 346(1), 380(3), 415(2), 435(4), 469(7), 484(9), 532(4, br), 582(4), 608(3), 732(2), 756(58, s), 786(16), 816(0), 846(1), 876(7), 896(10), 913(14), 935(9), 947(2), 981(3, d), 999(6), 1036(26, s), 1056(21), 1084(23), 1106(9), 1136(13), 1158(5), 1177(25, b), 1197(22, b), 1215(18, b), 1259(21), 1299(3), 1311(24), 1350(21), 1359(15), 1441(50), 1458(58), 2847(200), 2864(250, br, b), 2901(210, br, b), 2918(230, br, b), 2947(220, br, b), 2963(200, br, b).

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* Notations of the Raman lines: br – broad; d – diffuse; s – sharp; b – the line is situated against a background of substantial intensity.

Cis-1-ethyl-4-tert-butylcyclohexane (Cis-II). Cis-II was produced from 1-ethyl-4-tert-butylbenzene [9] by hydrogenation in a rotating autoclave at an initial hydrogen pressure of 150 atm and 150° in the presence of platinized charcoal, activated by chloroplatinic acid. In view of the small difference between the boiling points of the stereoisomers ($\Delta t = 0.2°$), they were separated by the new thiourea method [5, 6]. Two portions of the cis-isomer with the following properties were obtained in this way: portion (A) [5]: bp 123.7° (60 mm) and 208.4° (760 mm); freezing point −41.8°; n_D^{20} 1.4530; d_4^{20} 0.8253; degree of purity 97.9%. Portion (B) n_D^{20} 1.4525; d_4^{20} 0.8232; degree of purity 86.8%. In both cases the only impurity is the trans-isomer. Portion (A) was used to study the IR spectra; in view of its small amount, portion (B) had to be used for the Raman spectra.

Raman Spectrum ($\Delta\nu$, cm^{-1}): 190(0), 215(1), 242(2, br), 263(3), 274(6, d, br), 302(1), 342(13, br), 362(2, d), 378(3, d), 396(2, d), 413(1), 441(5), 479(4), 501(2), 524(17), 593(1), 621(40), 673(1), 752(50), 782(4), 798(1), 813(25, s), 823(26, s), 901(10), 925(45), 956(0), 997(12), 1033(10), 1038(30), 1052(23, s), 1076(3, p), 1094(2, d), 1130(8), 1161(8), 1188(28, s), 1207(3), 1224(23), 1237(28), 1264(2, d), 1276(27), 1286(1, d), 1301(10), 1309(7, d), 1340(10, d), 1351(18, d), 1438(56), 1457(10, b), 1468(34), 2658(10, d), 2672(7, d), 2715(15, d), 2730(8, d), 2851(120, d, b), 2870(150, d, b), 2907(250, b), 2944(180, b), 2965(190, br, b).

Trans-1-ethyl-4-tert-butylcyclohexane (Trans-II). Trans-II was produced together with the preceding compound and separated by the thiourea method. Properties [6]: bp 123.9° (60 mm) and 208.6° (760 mm); freezing point −46.9°; n_D^{20} 1.4479; d_4^{20} 0.8128; degree of purity 97.1% (the only impurity is the cis-isomer).

Raman Spectrum ($\Delta\nu$, cm^{-1}): 181(0), 196(0), 211(0), 236(0), 256(10, d, br), 283(8, d, br), 297(0), 342(5, d), 343(7, d), 381(2), 397(2), 420(1), 444(8, br), 461(4), 478(17), 506(20), 531(3), 546(1), 566(16), 591(0), 609(0), 625(0), 727(1), 751(105, s), 764(4), 785(8), 803(10, s), 813(2), 827(3), 843(1), 860(8), 904(1, d), 924(28), 931(29), 971(0), 998(4, d, br), 1028(2, d), 1042(50), 1066(3, d), 1090(10, d), 1100(7, d), 1140(8), 1156(7), 1170(0, d), 1192(23), 1210(15), 1237(32), 1268(28), 1306(8), 1317(6), 1344(13), 1360(30), 1445(50, br), 1463(35, d), 2626(5, d, br), 2673(15, d), 2718(20, d, br), 2847(260, b), 2883(120, b), 2910 (250, b), 2942(250, b), 2970(240, br, b).

Cis-1-ethyl-4-tert-amylcyclohexane (Cis-III). Cis-III was produced by hydrogenation of 1-ethyl-4-tert-amylbenzene [9] under the conditions indicated for the production of (cis-II). Since hydrogenation proceeded with difficulty, it was brought to completion in three operations, analogously to compound (I) (see above). The stereoisomers were separated by the thiourea method. Properties [5]: bp 121.0° (25 mm) and 233.9° (760 mm); n_D^{20} 1.4594; d_4^{20} 0.8380; degree of purity 98.8%. The Raman spectrum was not obtained.

Trans-1-ethyl-4-tert-amylcyclohexane (Trans-III). Trans-III was produced together with the preceding compound and separated by the thiourea method [5]. Properties: bp 121.5° (25 mm) and 233.9° (760 mm); n_D^{20} 1.4553; d_4^{20} 0.8282; degree of purity 97.6% (the only impurity is the cis-isomer). The Raman spectrum was not obtained.

DISCUSSION OF RESULTS

Table 1 presents the frequencies of the IR bands and Raman lines observed in the interval 600-650 cm^{-1} in the spectra of the compounds studied. Compounds in whose spectra sufficiently intense IR bands and Raman lines are present in this region were assigned the cis-configuration on the basis of the previously observed patterns [1, 2].

TABLE 1. Frequencies (cm^{-1}) of the Characteristic Lines and Bands in the Spectra of 1,4-Dialkylcyclohexanes

Compound	cis		trans	
	IR	Raman	IR	Raman
I	629 (m) 633 (m)	625 (16, s) 634 (12, s)	610 (v. w)	625 (0)
II	623 (m)	621 (40)	620 (v. w)	625 (0)
III	620 (m. db)	Not investigated	615 (w)	Not investigated

Note: m − medium, db − double; s − sharp; w − weak; v.w − very weak.

In the spectra of the other stereoisomers, the IR bands and Raman lines are very weak or absent altogether. On this basis we assigned the trans-configuration to them [1, 2].

The characteristic band in the IR spectra of compounds (I) and (III) (Fig. 1) takes the form of a doublet, just as in the spectrum of cis-1-methyl-4-tert-amylcyclohexane [2]. This peculiarity is probably due to the presence of rotational isomers, arising in the rotation of the tert-amyl or 1,1-dimethylpentyl radical around the equatorial C–C bond. In the case of the tert-butyl radical, all the conformations arising in this rotation are identical. Correspondingly, the characteristic bands in the IR spectra of 1-methyl-4-tert-butylcyclohexanes and compounds (II) are single.

CONCLUSIONS

1. The vibrational spectra (IR and Raman) of stereoisomeric 1-methyl-4-(1,1-dimethylpentyl)-, 1-ethyl-4-tert-butyl-, and 1-ethyl-4-tert-amylcyclohexanes, synthesized for the first time, were investigated.

2. On the basis of the previously found spectroscopic characteristic, the cis- and trans-configurations were assigned to the stereoisomers.

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