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

COMMUNICATION 2. 1-n-ALKYL-4-SEC-ALKYL- AND 1-n-ALKYL-4-TERT-ALKYLCYCLOHEXANES

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In a series of 1,4-dialkylcyclohexanes we studied the vibrational spectra of compounds with greatly differing conformational volumes of the radicals [1, 2], as well as compounds with the same hydrocarbon radicals [3]. In the vibrational spectra of all the cis-1-methyl-4-alkylcyclohexanes studied, there is a comparatively intense IR band at Raman line in the region of 600-650 cm^{-1}. In the spectra of the trans-isomers these bands and lines either are absent entirely, or are very weak. This agrees with the fact that in the latter hydrocarbons, both radicals are in a diequatorial position, since their diaxial arrangement is too energetically unprofitable.

In the spectra of the symmetrical 1,4-dialkylcyclohexanes studied [3], similar patterns were observed. Only in the IR spectra of stereoisomeric bis-(1-ethylpropyl)- and bis-(1-propylbutyl)-cyclohexanes is a deviation detected: for the stereoisomers that are recognized as trans-forms according to the Raman spectra, weak IR bands in the interval characteristic of the cis-forms were also observed. In view of this, an investigation of the spectra of stereoisomers of 1-methyl-4-(1-ethylpropyl)-cyclohexane (I), synthesized for the first time, the ethylpropyl radical which most likely occupies an equatorial position, was of special interest. The peculiarities of the spectra of these cis- and trans-isomers could be used to consider the nature of the deviation from the general principle observed in [3].

We also studied the vibrational spectra of two more pairs of newly synthesized stereoisomeric dialkylcyclohexanes: 1-n-propyl-4-isopropyl-(II) and 1-n-butyl-4-tert-butylcyclohexanes (III).

EXPERIMENTAL SECTION

The conditions of obtaining the spectra were the same as in [4, 5].

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	632 m	630 (13)	629 m	608 (3)
	649 m	648 (9)		
II	631 m	631 (26)	—	602 (1)
III	626 m	621 (21)	—	624 (1)

The IR absorption spectra in the region of 450-3100 cm^{-1} are cited in Figs. 1 and 2, while the frequencies and intensities of the Raman spectra are given in the text.

All the hydrocarbons studied, just like those described in our previous communication [2], were synthesized by hydrogenation of the corresponding dialkylbenzenes, while the mixture of stereoisomers obtained was separated either by precise fractional distillation or by the new thiourea method [6, 7], permitting the separation of stereoisomers even if they both form adducts with thiourea. The constants are given for each hydrocarbon; the boiling points under vacuum are experimental, while the values calculated from the experimental data with the aid of the Dreisbach

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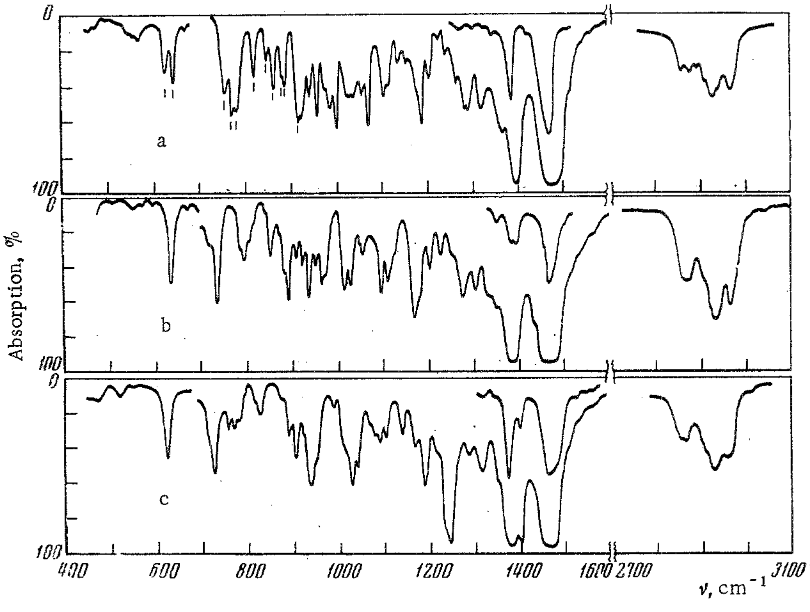

Fig. 1. IR spectra of cis-isomers: a) 1-methyl-4-(1-ethylpropyl)-cyclohexane: b) 1-n-propyl-4-isopropylcyclohexane; c) 1-n-butyl-4-tert-butylcyclohexane.

tables [8] are cited for 760 mm. At all stages of the synthesis and separation, measures were taken so that the purity of the preparations was as high as possible.

cis-1-Methyl-4-(1-ethylpropyl)-cyclohexane. Produced from p-(1-ethylpropyl)-toluene [9] by hydrogenation on Pt-charcoal (20% Pt) in a flow-type system with a volume velocity 0.2 h^{-1} in a stream of hydrogen at atmospheric pressure and 150°. The mixture of stereoisomers obtained, after freeing from the remains of the aromatic hydrocarbon by chromatography on silica gel, was separated by continuous multi-day round-the-clock distillation on a column with an efficiency of 100 theoretical plates. The distillation was conducted under a vacuum of 7-10 mm with a reflux ratio 200-250; the distillate was collected in portions of 3-4 g; a total of 42 fractions were collected. The fractions were analyzed on a capillary chromatograph, and those possessing a degree of purity no lower than 99.0% were combined. Properties [9]: bp 96.45° (17.5 mm); 214.1° (760 mm); n_D^{20} 1.4540; d_4^{20} 0.8276; degree of purity ~99.8%.

Raman spectrum* ($\Delta\nu$, cm^{-1}): 184(7), 202(1), 216(5), 245(3), 262(1), 282(3), 307(10, br), 335(2), 354(2), 371(5, d), 377(4), 407(1), 426(2), 444(6), 461(5), 479(3), 491(1), 504(2), 547(3, br), 572(4, br), 599(3), 630(13), 648(9), 670(2), 706(3), 728(1), 747(2), 764(43), 778(20), 809(8), 825(3), 838(12), 854(10), 875(1), 907(12, br), 925(4), 945(6), 963(5), 974(17), 982(3), 1008(7), 1028(12), 1039(20, br), 1058(30), 1088(15, d, br), 1103(12, d, b), 1119(10, d), 1128(7, d), 1151(17, br), 1171(14), 1192(17), 1207(11), 1232(9), 1247(3, d), 1263(28, br), 1288(8, d), 1302(4, d), 1318(13), 1344(15), 1363(10), 1437(60), 1447(30, d, b), 1465(50, b), 2848(230, b), 2873(210, b), 2903(230, b), 2931(280, b), 2960(180, b).

trans-1-Methyl-4-(1-ethylpropyl)-cyclohexane. Produced together with the cis-isomer and separated from it by fractional distillation on a column (see above). Properties [9]: bp 95.55° (17.5 mm); 213.0° (760 mm); n_D^{20} 1.4478; d_4^{20} 0.8133; degree of purity 99.8%.

Raman spectrum ($\Delta\nu$, cm^{-1}): 186(1), 216(0), 230(1), 246(2), 269(4, d), 286(7, d), 300(10, d), 381(3, d), 392(0), 425(1), 443(11), 466(9), 477(10), 486(1), 498(2), 513(5), 547(2), 592(1), 629(2), 653(0), 742(29), 747(6), 766(19), 777(20, br), 801(1), 823(2), 836(2), 860(6), 886(5), 901(4), 911(10), 942(5), 957(3), 994(9, b), 1005(8, b), 1019(3, d, b), 1038(25), 1066(26), 1074(15), 1099(6), 1153(22), 1172(26), 1222(3), 1236(5), 1250(26), 1261 (4), 1287(3), 1304(12), 1316(3), 1346(24), 1359(15), 1378(2), 1442(33, br), 1455(60), 2843(200, b), 2871(230, br, b), 2910(200, d, b), 2926(280, br, b), 2955(160, d, b).

cis-1-n-Propyl-4-isopropylcyclohexane. Produced by the hydrogenation of 1-n-propyl-4-isopropylbenzene [9] under the same conditions as those used for the production of the isomers of (I) (see above).

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

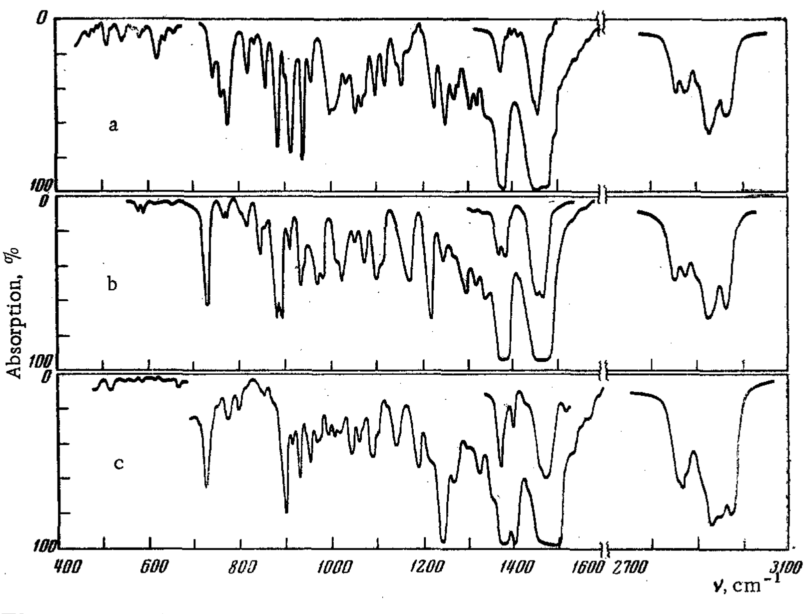

Fig. 2. IR absorption spectra of trans-isomers (the names of the hydrocarbons and notations are the same as in Fig. 1).

After freeing from residues of aromatic hydrocarbon by chromatography on silica gel, the stereoisomers were separated by the thiourea method. Properties [9]: bp 95.2° (16 mm); 216.1° (760 mm); n_D^{20} 1.4502; d_4^{20} 0.8190; degree of purity > 99%.

Raman spectrum ($\Delta\nu$, cm^{-1}): 191(2), 240(3), 276(1), 294(3), 312(4), 345(5), 352(2), 387(4), 398(2), 408(3), 429(2), 444(4), 473(6), 500(3), 537(1), 586(0), 631(26), 675(3), 722(3), 737(5), 783(23), 794(28), 813(3), 832(2), 847(12), 854(7), 889(10), 904(5), 922(3), 935(10), 951(13), 968(4), 981(2), 993(3), 1010(15 v.br. band), 1021(17 v. br), 1033(18v.br band), 1053(15v. br band), 1067(12v. br band), 1106(11,d), 1118(14, d), 1134(5), 1154(15), 1168(20), 1194(17), 1221(5), 1242(8), 1266(30), 1295(20), 1323(10, d), 1349(13, d), 1363(5, d), 1442 (78), 1461(60), 2848(260, br, b), 2866(320, b), 2908(300, d, b), 2935(320, d, br, b), 2963(220, br, b).

trans-1-n-Propyl-4-isopropylcyclohexane. Produced together with the cis-isomer and separated from it by the thiourea method. Properties [9]: bp 95.3° (16 mm); 216.3° (760 mm); n_D^{20} 1.4458; d_4^{20} 0.8080; degree of purity > 99%.

Raman spectrum ($\Delta\nu$, cm^{-1}): 200(5, br), 223(3), 234(10), 255(15), 293(1, b), 321(0), 367(2, br), 407(2), 438(5), 458(2, b), 477(12), 498(8), 537(0), 585(0), 602(1), 721(1), 738(8), 766(30), 776(25), 784(17), 813(6, d), 828(2, d), 852(7), 867(5), 888(9), 900(3, d), 916(2, d), 956(6, d), 973(2, d), 989(3, d), 1018(15, br), 1032(23, br), 1059 (12, d), 1069(18, b), 1080(15, d), 1103(7, d), 1119(6, d), 1149(1, d), 1159(22), 1169(27, 1192(1, d), 1213(3, d), 1249(30), 1270(10), 1296(17), 1318(7), 1336(12), 1359(23), 1440(52), 1461(45), 2843(250, b), 2871(230, b), 2937(230, b), 2963(160, b).

cis-1-n-Butyl-4-tert-butylcyclohexane. Produced from 1-n-butyl-4-tert-butylbenzene [10] by hydrogenation, just as in the case of 1-ethyl-4-tert-butylcyclohexanes [2]. A mixture of the stereoisomers, freed of residues of aromatic hydrocarbon by chromatography on silica gel, was separated by the thiourea method. Since the cis-isomer contains not only a small amount of the trans-isomer, but also 2.5% of an extraneous impurity, it was additionally redistilled on a column with an efficiency of 25 theoretical plates with a reflux ratio of 50. Properties [10]: bp 116.6° (12 mm); 250.5° (760 mm); freezing point –34.6°; n_D^{20} 1.4556; d_4^{20} 0.8281; degree of purity 98.5% (the only impurity is the trans-isomer).

Raman spectrum ($\Delta\nu$, cm^{-1}): 204(3, d), 278(6, d, br), 340(15), 355(9, d), 382(3), 414(1), 444(9), 482(3, br), 524(14), 625(21), 724(1), 736(1), 755(25, s), 766(9), 783(10), 815(15), 822(13), 830(11), 869(8), 887(6), 904(9), 917(8), 927(26), 950(10), 982(4), 1013(12), 1037(28), 1059(12), 1064(15), 1086(11, b), 1099(8, d, b), 1130(10), 1157(7, d), 1172(5, b), 1183(11, b), 1205(3), 1223(22), 1233(22), 1250(1), 1272(24, s), 1304(16), 1339(14), 1346(17), 1361(3), 1436(50), 1451(15, b), 1464(42), 2852(190), 2872(170, b), 2899(130, b), 2905(250, b), 2938(220, b), 2961(200, b).

trans-1-n-Butyl-4-tert-butylcyclohexane. Produced together with the cis-isomer and separated from it by the thiourea method. Properties [10]: bp 118.8° (12 mm); 252.0° (760 mm); freezing point –35.1°; n_D^{20} 1.4521; d_4^{20} 0.8191; degree of purity 99.3%.

Raman spectrum ($\Delta\nu$, cm^{-1}): 221(24, br), 238(8), 274(5), 300(3), 315(4), 347(10), 391(3), 419(4), 447(4), 477(10), 517(11, br), 526(3), 565(1), 587(14), 624(1), 715(1), 726(3), 735(2), 756(74), 773(8), 786(7), 798(10), 827(3), 845(9), 867(8), 896(8), 914(9), 929(30), 944(5), 962(1), 985(5), 1041(40), 1061(11), 1087(15), 1103(12), 1141(11, br), 1175(9), 1185(11), 1209(15), 1235(35), 1267(26), 1285(5), 1301(14), 1317(7), 1342(11), 1358(24), 1440(58), 1464(47, d), 2844(250), 2853(170, b), 2869(120, b), 2893(150, b), 2910(220, b), 2940(220, b), 2964 (180 b).

DISCUSSION

Table 1 presents the frequencies of the IR bands and Raman lines, observed in the interval 600-650 cm^{-1} of the spectra that we studied. Just as before [1-3], all the stereoisomers can be divided into two groups: in the spectra of one of them there are comparatively intense lines and bands in the indicated region, sometimes double (see Fig. 1), while in most of the spectra of the second group they are absent or weak (see Fig. 2). We ascribed a cis-configuration to all the stereoisomers of the first group, in accord with the earlier conclusions, and a trans-configuration to the stereoisomers of the second group.

An exception is the IR spectrum of the isomer of (I) to which we ascribed a trans-form on the basis of the Raman lines. It contains a band at 629 cm^{-1} of medium intensity. Its position is close to one of the two bands in the spectrum of the cis-isomer (see Table 1). These bands may be associated with vibrations of the equatorial 1-ethylpropyl radical in both isomers. As has already been stated above, the same deviations also exist in the IR spectra of bis-1,4-(1-ethylpropyl)- and bis-1,4-(1-propylbutyl)-cyclohexanes [3]. Therefore, the possibility remains that the bands under discussion in the IR spectra of their trans-isomers are also due to the vibrations of the equatorial radicals. The following evidence may be cited in support of these hypotheses: in the same characteristic region of the spectrum of (1-ethylpropyl)-cyclohexane there is an IR band at 616 cm^{-1} and a Raman line 608 cm^{-1},* which are considerably more intense than in the spectra of the other known monoalkylcyclohexanes [11].

Since the concentration of a-conformation in methylcyclohexane is negligible [12], for the 1-ethylpropyl radical, which has a far greater conformational volume, this conformation, all the more, can be neglected. Thus, the great intensity of the band under discussion is probably associated with the vibration characteristic of the 1-ethylpropyl radical.

CONCLUSIONS

1. The principles found earlier, characterizing the cis- and trans-isomers of 1,4-dialkylcyclohexanes, have been confirmed on three pairs of new representatives of this series.

2. The IR and Raman spectra of cis- and trans-isomers of 1-methyl-4-(1-ethylpropyl)-, 1-n-propyl-4-isopropyl-, and 1-n-butyl-4-tert-butylcyclohexanes are published for the first time.

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*The synthesis and spectra of this compound will be published later.

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