

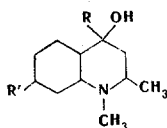
DETERMINATION OF THE THREE-DIMENSIONAL ORIENTATION
OF THE HYDROXYL GROUP IN STEREOISOMERIC 1,2,7-TRIMETHYL-
AND 1,2-DIMETHYL-7-*tert*-BUTYLDECAHYDRO-4-QUINOLOLS
AND THEIR 4-ETHYNYL-SUBSTITUTED DERIVATIVES
BY IR SPECTROSCOPY

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The three-dimensional orientation of the hydroxyl group in stereoisomeric 1,2,7-trimethyl- and 1,2-dimethyl-7-*tert*-butyldecahydro-4-quinolols and their 4-ethynyl-substituted derivatives was established by IR spectroscopy. The possibility of a twist conformation of the heteroring in 1,2,7-trimethyl- and 1,2-dimethyl-7-*tert*-butyldecahydro-4-quinolols with an equatorial hydroxyl group is shown.

The present communication is devoted to the establishment of the orientation of the hydroxyl group in stereoisomeric alcohols I-XVIII.



I-XVIII

I-X R = H; XI-XVIII R = C≡CH; I-V, XI-XIV R' = CH₃; VI-X V-XVIII R' = C(CH₃)₃

The secondary alcohols were synthesized by reduction of individual 1,2,7-trimethyl- or 1,2-dimethyl-7-*tert*-butyldecahydro-4-quinolones. Alcohols I and II, III and IV, VI and VII, and VIII and IX (see Table 1) are epimeric pairs with respect to the 4 position, each of which was obtained from the corresponding individual decahydroquinolone isomer. Decahydroquinolols V and X were each synthesized from ketones of the *cis* series. Acetylenic alcohols XI-XVIII were obtained by ethynylation of the individual ketones or mixtures of them, during which only one alcohol isomer is formed from each ketone.*

The bands of the C-O and O-H stretching vibrations can be used for the conformational assignments in the cyclic alcohols. It is known [1] that an equatorial OH group in alicyclic alcohols has a higher ν_{C-O} frequency and a lower ν_{O-H} frequency than an axial OH group. Information regarding the orientation of the OH groups in cyclohexanols and other cyclic alcohols has also been established by analysis of the contour of the ν_{O-H} band [2, 3], according to which the OH-stereoisomeric alcohols differ not only with respect to their frequencies but also with respect to other parameters of the band — the half-width, symmetry, molar extinction coefficient, and integral intensity.

In addition, the three-dimensional orientation of the hydroxyl group can be established from an examination of the form of the band of the stretching vibration of the C-O bond of acetoxy derivatives of cyclic alcohols. As previously shown in [4], one band at 1200-1260 cm⁻¹ was observed in the spectra of acetates of equa-

*A detailed description of the synthesis of the investigated compounds is given in [9].

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TABLE 1. Basicity Constants and $\nu_{\text{O-H}}$ Bands of Stereoisomeric Alcohols and $\nu_{\text{C-O}}$ Bands of Their Acetates

Alcohol	Isomer	mp, °C	pK	$\nu_{\text{O-H}}, \text{cm}^{-1}$	$\nu_{\text{C-O}}, \text{cm}^{-1}$
1,2,7-Trimethyldecahydro-4-quinolol	I	155—156	10.54	3632	1242, 1263
	II	168—169	9.86	3628, 3600 (shoulder)	1243
	III	142—143	9.87	3625, 3602	1246
	IV	108—109	10.46	3632	1225, 1236
	V	—	—	3613	1235
1,2-Dimethyl-7-tert-butyldecahydro-4-quinolol	VI	167—168	10.06	3631	1234, 1255
	VII	178—179	9.25	3628, 3605	1237
	VIII	170—171	9.94	3628, 3605	1237
	IX	104—105	10.43	3631	1225, 1233
	X	—	—	3612	1235
1,2,7-Trimethyl-4-ethynyldecahydro-4-quinolol	XI	126—127	9.73	3615	1226, 1235
	XII	118—119	9.70	3613	1224, 1233
	XIII	129—130	9.71	3615	1223, 1232
	XIV	109—110	9.72	3614	1222, 1233
1,2-Dimethyl-7-tert-butyl-4-ethynyldecahydro-4-quinolol	XV	102—103	9.82	3615	1220, 1232
	XVI	99—100	9.80	3614	—
	XVII	107—108	9.79	3615	1220, 1232
	XVIII	89—90	9.81	3614	1230, 1260

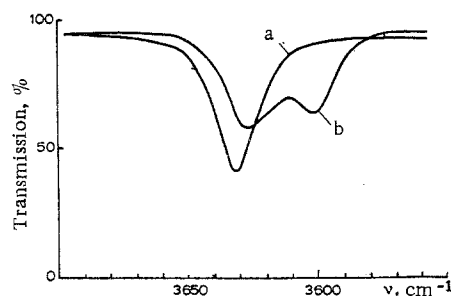


Fig. 1. Contours of the $\nu_{\text{O-H}}$ band characteristic for stereoisomers I, IV, VI, and IX (a) and II, III, VII, and VIII (b).

torial 1,2,4-substituted decahydro-4-quinolols, and two or three bands were observed in the same region in the spectra of acetates of axial alcohols. The noted differences were explained by free rotation of the acetoxy group when it is equatorially oriented, whereas its rotation is retarded when it is axially oriented owing to steric interaction with the meta-axial protons, which leads to the existence of several rotameric forms [5].

In the present study we analyzed the contours of the $\nu_{\text{O-H}}$ bands of the alcohols and the $\nu_{\text{C-O}}$ bands of their acetates to determine the three-dimensional orientation of the hydroxyl group in 1,2,7-trimethyldecahydro-4-quinolols, 1,2,7-trimethyl-4-ethynyldecahydro-4-quinolols, and their tert-butyl analogs. Unfortunately, the analysis of the $\nu_{\text{O-H}}$ band reduced mainly to the determination of its frequency, inasmuch as measurement of the other parameters of this band did not enable us to ascertain definite principles of their change as a function of the orientation of the OH group.

As seen from Table 1, in the series of stereoisomeric secondary 1,2,7-trimethyl- and 1,2-dimethyl-7-tert-butyldecahydro-4-quinolols, isomers I and IV and VI and IX are distinguished by the highest $\nu_{\text{O-H}}$ frequency — 3632 and 3631 cm^{-1} , respectively. A doublet absorption band is present in the spectra of their acetates in the region of the stretching vibrations of the C—O bonds. A lower $\nu_{\text{O-H}}$ frequency (3628 and 3625 cm^{-1}) corresponds to alcohols II, III, VII, and VIII, and their acetates have singlet $\nu_{\text{C-O}}$ bands. On the basis of this, an axial orientation of the OH group should be assigned to stereoisomers I, IV, VI, and IX, and an equatorial orientation should be ascribed to stereoisomers II, III, VII, and VIII. The basicity constants (see Table 1) are in good agreement with these results, and this is also in agreement with concepts regarding the more basic nature of an axial group (see, for example, [6, 7]).

One's attention is drawn to the presence in the spectra of alcohols II, III, VII, and VIII, which we characterized as equatorial alcohols, of an additional band or a shoulder at 3600–3605 cm^{-1} (Fig. 1b). This fact should, in our opinion, be explained by the shift of the band at 3628 cm^{-1} due to the formation of a weak intramolecular hydrogen bond between the OH group and the free electron pair of the nitrogen atom. This sort of association is possible in the twist conformation of the heteroring of the two-ring system, which,

judging from the spectrum, is in equilibrium with the chair conformation. The small shift ($\Delta\nu = 15 \text{ cm}^{-1}$) of the band in the spectrum of 3- β -granatol was similarly explained [2], whereas the formation of an intramolecular hydrogen bond in the same compound in the classical boat conformation led to a more substantial shift of the band ($\Delta\nu = 238 \text{ cm}^{-1}$) [8] as a result of close approach of the atoms making up the bond. It is evident from an examination of molecular models that an intramolecular hydrogen bond is possible only in the case of an equatorial orientation of the hydroxyl group. The presence in the spectrum of a band or shoulder at $3600\text{--}3605 \text{ cm}^{-1}$ may therefore serve as an additional indication of an equatorial three-dimensional orientation of the OH group.

As we have already noted above, the isomers of alcohols V and X, in contrast to other secondary decahydroquinolols, were obtained from the cis-decahydroquinolones. From the singlet form of the band at 1235 cm^{-1} in the spectra of the acetates, an equatorial orientation of the hydroxyl group should be assigned to them. However, a symmetrical $\nu_{\text{O-H}}$ band is characteristic for these alcohols. It is apparent that the form of fusion of the decahydroquinoline ring has a substantial effect on inversion of the heteroring. One should also note the anomalously low $\nu_{\text{O-H}}$ frequency in the spectra of isomers V and X.

The stereoisomers of acetylenic alcohols XI-XVIII differ little from one another with respect to the frequencies of the stretching vibrations of the OH groups ($3613\text{--}3615 \text{ cm}^{-1}$), whereas their corresponding acetates are characterized by doublet $\nu_{\text{C-O}}$ bands, and this makes it possible to assign an axial conformation of the hydroxyl group to these isomers. The close basicities may also indicate an identical orientation of the OH groups in alcohols XI-XVIII.

EXPERIMENTAL

The spectra of the investigated compounds were measured at room temperature with a UR-20 spectrometer at a scanning rate of 25 cm^{-1} . The spectral slit width at 3600 cm^{-1} was 4.9 cm^{-1} , as compared with 4.5 cm^{-1} at 1250 cm^{-1} . The spectra of CCl_4 solutions of the alcohols ($2\text{--}3.5 \cdot 10^{-3}$ mole/liter) were recorded at an absorbing-layer thickness of 2 cm; the spectra of the esters of the secondary alcohols were recorded in the form of thin films between KBr windows. The spectra of CCl_4 solutions and KBr pellets of the esters of the acetylenic alcohols were recorded.

The basicity constants of the stereoisomeric alcohols were determined by potentiometric titration of 0.01 N solutions of their hydrochlorides with a 0.5 N solution of NaOH at 25° . The accuracy in the measurements was ± 0.05 .

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