Tetrahedron. Vol. 24, pp 4759 to 4777 Pergamon Press 1968 Printed in Great Britain

INFRARED SPECTRAL CONSEQUENCES OF CONFORMATIONAL HETEROGENEITY IN SATURATED ALCOHOLS

L. JORIS,* P. VON RAGUÉ SCHLEYER and E. ŌSAWA

Frick Chemical Laboratory, Princeton University, Princeton, N.J. 08540

((*Received in USA* 16 *December* 1967, *accepted for publication* 3 *February* 1968)

Abstract—The best explanation for the doublet character of IR OH stretching absorptions of many saturated alcohols is conformational heterogeneity. According to this theory each C—O rotational isomer (rotamer) gives rise to a symmetrical OH absorption. Therefore, as predicted, molecules with only one minimum energy rotamer have symmetrical OH spectra. When the absorption frequencies of two or more rotamers are different, the experimentally observed summation spectra are ordinarily asymmetrical. The main class of compounds studied was cyclohexanol derivatives. Asymmetrical spectra were decomposed by digital computer into two symmetrical component bands, assumed to have Lorentzian band shapes, and these bands were remarkably constant for a given rotamer type and did not depend on whether the alcohols were secondary or tertiary. 'Absorption bands near 3624 cm^{-1} in tertiary axial cyclohexanols were assigned to a type of rotamer in which the OH bond lies over the cyclohexane ring. To rationalize the symmetrical OH absorptions of secondary axial cyclohexanols, it was previously suggested that this type of rotamer was absent due to steric repulsion of the OH hydrogen with the 3,5-diaxial hydrogens of the ring. We favor an alternative explanation: that the rotamers with the OH bond over the ring and with the OH bond pointing away from the ring are both present, but have about the same adsorption frequency.

THE most characteristic and most often cited evidence for intramolecular hydrogen-bonding is the observation of two concentration independent OH stretching absorptions in the IR spectrum.[1] However, the OH absorptions of saturated alcohols, obviously incapable of intramolecular hydrogen bonding, may also have doublet character.[2–13] Compounds with weak intramolecular hydrogen-bonds, e.g. allyl alcohols,[14,15] benzyl alcohols[9,14,16,17] and cyclopropylcarbinols,[14,18] give IR spectral shifts comparable to those displayed by some saturated alcohols. In these cases, a convincing demonstration of the presence of intramolecular hydrogen-bonding is complicated considerably but is by no means impossible. The spectrum of the alcohol suspected of having an intramolecular hydrogen-bond is compared with that of a model saturated alcohol. In contrast to the spectrum of a model saturated alcohol, the spectrum of a compound forming a weak intramolecular hydrogen-bond will have the low frequency band displaced to lower frequencies and, in addition, the ratio of the intensity of the low frequency band to that of the high frequency band will be greater. Choice of an appropriate model saturated alcohol is, of course, crucial to the success of this type of analysis.

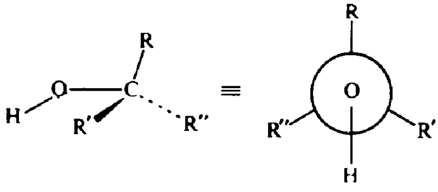
---

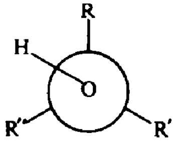
* National Science Foundation Cooperative Fellow, 1963–1964; National Institutes of Health Predoctoral Fellow, 1967–1968. Ph.D. Thesis, Princeton University, 1968.

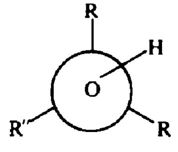
Because of our continuing interest in IR studies of hydrogen-bonding, we have examined the relation of the structures of saturated alcohols to the position and shape of their OH absorptions. Our aim was to gain sufficient understanding of this phenomenon so that we would be able to make reliable analyses of the spectra of weakly intramolecularly hydrogen-bonded alcohols, i.e. which portions of the observed curves were due to association and which portions to other factors.

Origin of doublet OH *character.* The origin of doublet OH character in saturated alcohols has been the subject of some controversy. Intermolecular association cannot be the cause, since the shapes of asymmetrical OH peaks are concentration independent.[4,5,7] Fermi resonance, suggested by Flynn *et al.*[4] as a possible explanation, was shown experimentally not to be responsible for doublet OH character. The asymmetrical band shape of the first overtone of the OH stretching vibration of 2-propanol was retained in the first OD overtone of deuterated 2-propanol.[5] The primary and secondary alcohols studied by Dalton *et al.*[7] all had the same band shapes in the fundamental as they did in the first overtone of the OH stretching vibration. In addition, the OH fundamental, the OH first overtone, and the OD fundamental stretching vibration of 4-heptanol[12] all had the same band shape. Fermi resonance cannot account for these observations, since it is exceedingly unlikely that other vibrations would couple with the fundamental and the first overtone in a way to produce OH or OD spectra all of similar appearance.

A third explanation is conformational heterogeneity:[2,5–9,13] the asymmetrical OH absorptions result from the superposition of two or more symmetrical bands, each due to a rotational isomer (rotamer) present in equilibrium. The barrier to rotation of the C—O bond in methanol is about 1 kcal/mole.[19] Approximately the same value was obtained from the determination of the barrier to rotation of the C—O bond in ethanol.[20] The minimum energy conformation in methanol has the OH hydrogen staggered with respect to the Me hydrogens,[21] and there are three such equivalent conformations of minimum energy. It is reasonable to expect the staggered conformations Ia, Ib and Ic in alkyl substituted alcohols,


Ia

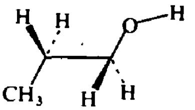

Ib


Ic

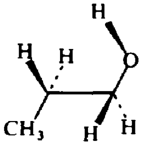
$RR'R''COH$, also to be energy minima and all to be significantly populated. When $R \neq R' \neq R''$ and $R \neq R''$ the three rotamers Ia, Ib and Ic are all different, and present different environments to the OH group. Hence, there should be three different symmetrical OH absorptions, corresponding to each of these rotamers, and the observed spectrum should be the composite of these bands.

According to the conformational heterogeneity hypothesis, when the R groups are identical, the experimental OH absorption must be symmetrical. Indeed the spectra of such alcohols, e.g. methanol,[2,5,6,7,12,22][*] t-butanol,[2,5,6,7,12,22] 1-adamantanol[22] and 1-hydroxybicyclo[2.2.2]octane,[22] are symmetrical. The converse is not necessarily true, since the addition of two or more peaks with different frequencies may also produce a symmetrical summation peak. Also, bands of different rotamers may fortuitously absorb at the same, or very nearly the same, position.

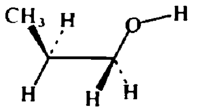
A fourth explanation is that the low frequency bands of certain saturated alcohols are due to a C—H … O intramolecular hydrogen-bond.[11,12] Krueger and Mettee[11] observed a partially resolved triplet OH absorption for 1-propanol[†] with maxima at 3639 cm^{-1}, 3633 cm^{-1} and 3627 cm^{-1}, and attributed these to conformers IIa, IIb, and IIc, respectively. Their spectrum is reproduced in Fig. 1. From the temperature dependence of the absorbances of the apparent peak maxima, the relative enthalpies for the equilibria between the conformers were calculated. Krueger and Mettee stated that "this treatment suffers from the disadvantage that the components of the bands overlap badly and therefore make contributions to the peak absorbances of the neighboring band(s)".[11] To illustrate this point, we had the spectrum of 1-propanol reproduced in the paper by Krueger and Mettee[11] decomposed by means of a Du Pont 310 Curve Resolver into three bands (Fig. 1).[‡] In the original spectrum, the 3633 cm^{-1} peak appears to be reasonably important, but in the decomposed spectrum, it is seen to be a very minor component. In other words, there is a great discrepancy between the peak heights of the minor bands in the reported and in the decomposed spectra. Krueger and Mettee[11] did not decompose their spectrum, but calculated ΔH's on the basis of these apparent peak heights. This procedure (as well as the claimed observation of three bands)[†] seems highly questionable to us. Based on these "ΔH measurements" Krueger and Mettee proposed that conformer IIc, said to give rise to the 3627 cm^{-1} band, was the most stable. The explanation offered was that a CH…O intramolecular hydrogen-bond between a Me hydrogen and the lone pair of electrons on oxygen stabilized this conformation.



IIa



IIb



IIc

---

[*] However, Flynn *et al.*[4] decomposed the OH spectrum of methanol into two bands. The minor band, which was found to comprise only 2–5% of the area of the major band,[4] is in our estimation insignificant. Even symmetrical absorptions may possess minor features of asymmetry.[13] Limitations of spectrophotometers and interferences due to atmospheric water are probable causes. None of the other references cited reported the presence of more than one band in the OH absorption of methanol.

[†] In contrast, we cannot repeat this observation and can detect but one maximum for the OH absorption of 1-propanol. Furthermore, such a triplet absorption, which would be quite unusual, was not mentioned by other investigators who also studied the OH absorption of 1-propanol.[1,4,6,8,12]

[‡] We wish to thank members of the Du Pont Instruments Products Division for this resolution. The typical band shape to be expected for symmetrical component bands was calibrated to be identical with the free OH absorption of p-fluorophenol.

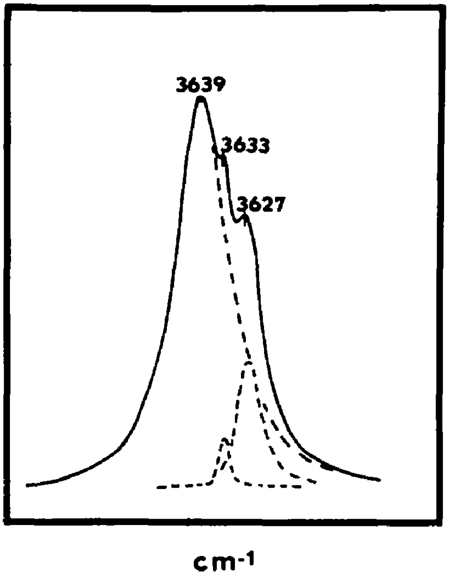
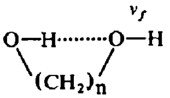
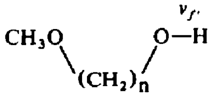


Fig. 1 —— Reproduction of the OH spectrum of 1-propanol shown in Ref. 11. - - - Spectral component bands as determined by a Du Pont 310 Curve Resolver.[26]

Similarly, Saier *et al.*[12] attributed the low frequency component bands of certain primary and secondary aliphatic alcohols to the OH absorptions of OH groups serving as a proton acceptors in CH...O hydrogen-bonds. The component bands of the OH absorptions of 4-heptanol and 1-heptanol were studied as a function of temperature, and from the data a negative enthalpy was calculated for the low frequency minor bands. Since a negative enthalpy is suggestive of an attractive interaction, hydrogen-bonding between a hydrogen on a γ C atom and the lone pair of electrons on the OH oxygen atom was postulated. Saier *et al.* admitted that their explanation for band asymmetry could not be comprehensive, because another phenomenon must be creating the doublet OH absorptions of alcohols, which have no γ alkyl groups *cis* to the OH oxygen, such as 2-propanol and certain cyclic alcohols.

We are skeptical of the hypothesis that the low frequency OH bands in saturated alcohols are due to CH ... O intramolecular hydrogen-bonds, since hydrogens on sp^3 hybridized C atoms lacking electronegative substituents should be incapable of functioning as proton donors in hydrogen-bonding.[23] The suggestion that a very weak CH...O hydrogen-bond lowers the OH stretching force constant[12] appears dubious, since a strong OH...O hydrogen-bond does not significantly alter the frequency of the "free" OH (ν_f); when the OH oxygen of a diol serves as proton acceptor, ν_f is essentially the same as $\nu_{f'}$ of the corresponding methoxy alcohol, where of course there can be no strong intramolecular hydrogen bond to the oxygen of the OH group.[24]





$n = 2\text{–}4$

Conformational heterogeneity seems to be the most reasonable of the explanations for the doublet character of the OH absorptions of many saturated alcohols and has received the greatest acceptance.[2, 5–9]

RESULTS AND DISCUSSION

The basic problem in analyzing the OH spectra of saturated alcohols is the asymmetrical band shapes usually observed. The best approach is to decompose such spectra into several symmetrical components. Frequently, the component bands may be the absorptions of C—O rotamers and hence have physical significance. The commonly employed methods for spectral decompositions use graphical separation,[25] an analog computer (notably the Du Pont 310 Curve Resolver)[26] and a digital computer.[27] In the latter method, which we have used, a symmetrical component band is represented by a suitable mathematical function, and the peak positions, peak heights, and band widths of a specified number of component bands are varied until the calculated summation spectrum is identical with the experimental one.

A Lorentz mathematical function adequately describes the shape of symmetrical experimental IR absorptions.[27] However, as Ramsay[28] first noted there generally is a discrepancy between a Lorentzian band and the "wings" of the experimental absorption band (Fig. 2). Since we used a Lorentz function to generate the component bands, our calculated spectra* usually did not exactly reproduce the experimental ones (Fig. 3).

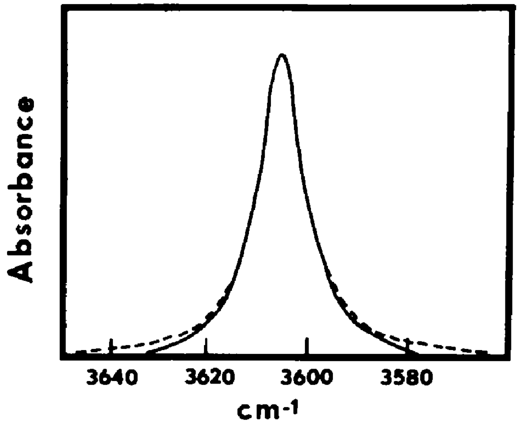


FIG. 2 —— Experimental OH absorption of *p*-fluorophenol; - - - Lorentzian band fitted to this experimental absorption by computer.

The accuracy of our spectral resolution method was checked by decomposing "spectra" artificially synthesized by the addition of two symmetrical experimental infrared absorptions and comparing the known band parameters with those calculated from the composite "spectra".[29] It was found that peak positions can be determined by the computer program more accurately than peak heights, which in turn can be determined more accurately than band widths. The calculated band

---

* A modified Stone program[27a] was employed. The component bands were simulated by a Lorentz function. A copy of our program and detailed instructions for its use may be found in the Ph.D. Thesis of L. J., Princeton University, 1968.

parameters of the smaller components always showed greater errors than those of the larger components. Furthermore, as the band separation decreased, the accuracy of the decomposition decreased.

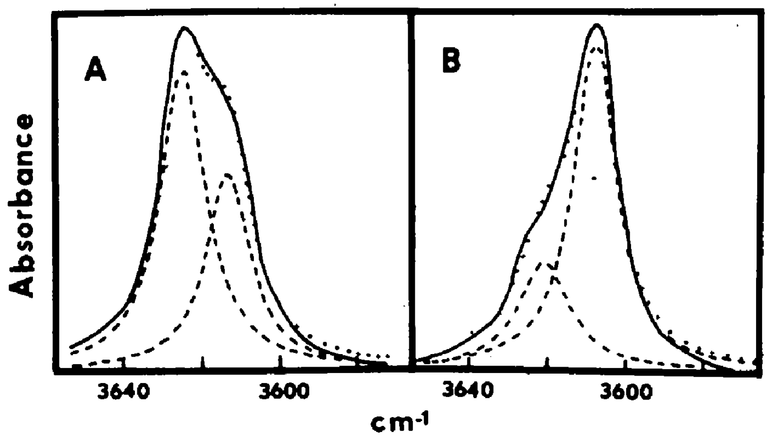


FIG. 3 Spectrum A, *trans*-9-decalol (2); spectrum B, *cis*-9-decalol (5). —— Experimental OH absorption; - - - calculated spectral component bands. . . . . . calculated spectrum.

Although the spectra of methanol, ethanol, 2-propanol and t-butanol have been analyzed several times previously, these spectra were re-examined in order to compare the band shapes, and especially the results of our method for spectral decomposition with those in the literature (Table 1). We confirmed prior observations that ethanol[2,5,6,10] and 2-propanol[5,6,10,12] have asymmetrical OH absorptions and that methanol and t-butanol have symmetrical ones. A comparison of the spectral decomposition data listed in Table 1, reveals reasonable agreement between the various determinations of peak positions and band widths. The band areas, by contrast, differ markedly in some instances. Our values are closest to those reported by Ōki and Iwamura.[6] This agreement is to be expected since only we and these investigators employed a Lorentz function to describe the component bands. The other investigators[4,7,8] spearated the experimental spectra into two symmetrical bands graphically. The graphical separation method is less satisfactory, because the component bands are assumed merely to be symmetrical and do not necessarily approximate the shapes of actual IR absorption bands.

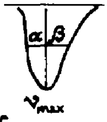
Ōki and Iwamura[6] are responsible for the interpretative method used in the present paper. The environment of the OH group in the three possible minimum energy rotamers of an alcohol is grouped according to type (Table 2). Type A has the OH hydrogen *gauche* to two H atoms; in type B, the environment of the OH hydrogen is one hydrogen and one Me group, while type C rotamers present two Me groups to the OH group. *The key assumption is that the* OH *frequency is determined primarily by the rotamer type, i.e. the immediate environment of the* OH *group and not by other structural features of the molecule.* The data in Table 2 show that this assumption is reasonable for methanol, ethanol, 2-propanol and t-butanol. The spectra of cyclic alcohols, which will be discussed subsequently, and additional acyclic examples[6,9] have provided further supporting evidence.

TABLE 1. SPECTROSCOPIC MEASUREMENTS OF THE OH STRETCHING ABSORPTIONS OF ACYCLIC SATURATED ALCOHOLS

			ν_{max} (cm^{-1})			Widths (cm^{-1})^c	
Compound	α/β^a	Ref.	Band 1	Band 2	A_1/A_2^b	Band 1	Band 2
Methanol	1·0	^{d}	3643			21	
		6	3644			22	
		7	3643			20	
Ethanol	0·8	^{d}	3637	3625	1·7	21	16
		6	3637	3627	1·8	18	19
		7	3636	3622	8·0	20	12
		4	3637	3627	7·7		
		8	3639	3624	11·0		
2-Propanol	0·7	^{d}	3627	3616	2·1	19	19
		6	3627	3617	1·7	14	26
		7	3626	3611	7·5	17	14
		4	3627	3614	14·0		
t-Butanol	1·0	^{d}	3616			18	
		6	3617			15	
		7	3616			16	

---

[a] The symmetry of a spectral band may be conveniently expressed as the ratio of the distances from the frequency at the absorbance maximum (ν_{max}) to the high (α) and low (β) frequency sides of the spectrum at half the maximum absorbance.[13]



[b] (Area of band 1)/(area of band 2).

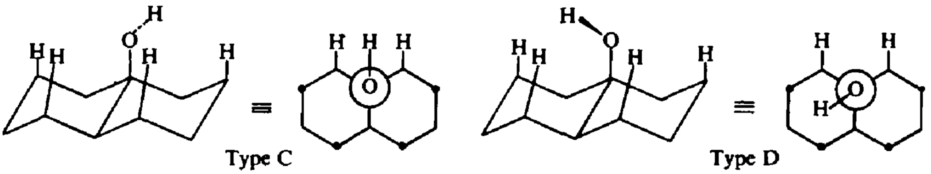
[c] Measured at half the maximum absorbance.

[d] This study.

Cyclic alcohols. A test of the hypothesis that only the local environment of the OH group determines its stretching vibrational spectrum is provided by comparisons in the cyclic series. 5α-Cholestan-5α-ol (**1**)[7] and *trans*-9-decalol (**2**, Fig. 3A) are molecules which differ greatly in overall structure, but nevertheless present approximately the same local environment to the OH group. Two rotamer types, C and D (Chart I;

CHART I

C—O Rotamers of *trans*-9-decalol,



C—O Rotamers of 5α-Cholestan-5α-ol

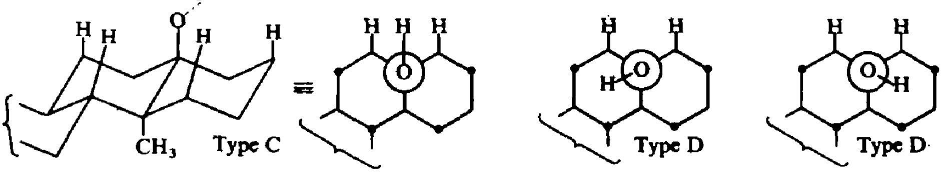
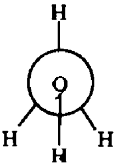
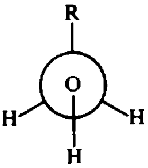
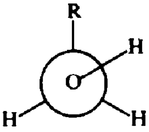
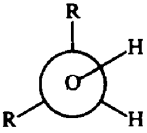
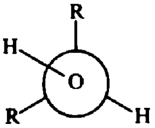
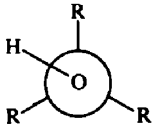


Table 2. Assignments of C—O Rotamers to O—H Component absorptions of acyclic alcohols[a]

Frequency range[b]	Type	Methanol	Ethanol	2-Propanol	t-Butanol
3644–3636 cm^{-1}	A				
3627 cm^{-1}	B				
3617 cm^{-1}	C				
		R = CH$_3$			

[a] Assignments of Ōki and Iwamura.[6]

[b] Taken from Table 1.

also see Chart II for a summary of rotamer types) are possible for both molecules. On this basis, one would expect approximately the same OH spectrum from **1** and **2**. This is actually the case. The spectrum of **1**, was reported by Dalton *et al.*[7] to be a clearly resolved doublet with a major band at 3629 cm^{-1} and a minor one at 3611 cm^{-1}. We find the spectrum of **2** to be a partially resolved doublet, which can be decomposed into a more intense band at 3625 cm^{-1} and a weaker one at 3613 cm^{-1}.

The problem of assignment of these bands to appropriate conformations, C or D, remains. Dalton *et al.*[7] used the superficially reasonable approach of assuming a relationship between the band intensity and the expected conformation population. For example, they assumed that rotamers of type D would be relatively unpopulated due to adverse nonbonded interactions between the OH hydrogen and the two axial hydrogens of the cyclohexane ring. On this basis, rotamer D could then be assigned to the band component (at 3611 cm^{-1} in **1**, and at 3613 cm^{-1} in **2**) with the weaker absorption; the more intense band components (at 3629 cm^{-1} in **1** and at 3625 cm^{-1} in **2**) would be attributed to type C rotamers.

Unfortunately, the matter is not as simple as this, and it seems to us more likely that the correct assignments are the reverse of those proposed by Dalton *et al.*[7] In the acyclic series, rotamers of type C (e.g. t-butanol, 3616 cm^{-1}) give bands more closely corresponding in position to the low frequency and not the high frequency components of **1** and **2**. Cyclic alcohols having only C type conformations provide even closer correspondence. Molecules in this class, such as 1-adamantanol (**3**) and 1-hydroxybicyclo[2.2.2]octane (**4**), give symmetrical bands at 3605 cm^{-1} and at

3608 cm^{-1}, respectively. Thus, on the basis of peak *positions*, it appears more reasonable to assign the 3611 cm^{-1} band of **1** and the 3613 cm^{-1} band of **2** to conformation C, and not to D.[7]

It is clear that there is a discrepancy in assignments based on component intensities, at least as interpreted by Dalton *et al.*,[7] and in component *positions*, as favored by us. Actually, a closer analysis of the relative intensities of the component bands lends further support to our assignments.

Two bands are present in the decomposed spectrum of *cis*-9-decalol (**5**; Fig. 3B). While the positions of absorption are about the same as those observed for **1** and **2**, *the relative intensities of the two components are reversed.* In **5**, the major intensity band, which we attribute to essentially equivalent conformations C, comes at 3608 cm^{-1}, while the minor component (due to D) has a maximum at 3621 cm^{-1}.

In comparing relative intensities of the high and low frequency components of an absorption band, a statistical correction for the number of equivalent conformations should be made. In **1** and **2** there are two conformations of Type D, and one of type C, but in **5** there are two type C and one type D arrangements. After these statistical corrections are made, relative intensity ratios of 1·3 and 1·5 (Table 3) are found for **2** and **5**, respectively, *provided our conformational assignments are used.* Using the reverse assignments, following Dalton *et al.*[7] these ratios would be 3·0 for **2** and 0·17 for **5**. This large discrepancy makes these assignments seem unreasonable, since not only the frequencies but also the intensities of bands in equivalent environments would be expected to be similar.

Further examples reinforce these arguments (Table 3). In particular, *trans*-4-t-butyl-1-methylcyclohexanol (**6**), with two C type and one D type conformations, gives component positions and relative intensities consistent with those of **2** and **5**. Interestingly, the epimer of **6**, *cis*-4-t-butyl-1-methylcyclohexanol (**7**), gave but a slightly asymmetrical* band ($\alpha/\beta = 1{\cdot}2$, Table 3), and no attempt at spectral decomposition was made. All conformations available to this compound are of type C, and the single band observed at 3611 cm^{-1} follows expectation.

The remaining cyclic alcohols upon which we report here are all secondary (Table 3). Such compounds have been investigated by Cole *et al.*[30] and by Aaron and Rader.[13] The latter group made the useful generalization that the OH absorptions of equatorial secondary cyclohexanols are generally asymmetrical (cf., the α/β ratios of about 0·6 for **8**, **9** and **10**, Table 3). In contrast, the absorptions of axial alcohols absorbed at higher frequencies than equatorial ones. Both of these groups of workers attributed the observed behavior to the absence of conformers of type D (which would have the hydroxyl hydrogen lying over the cyclohexane ring where it might interact unfavorably with the two axial ring hydrogens—the argument of Dalton *et al.*[7]).

Cole *et al.*[30] attributed the higher frequencies of axial alcohols to steric interaction of the OH oxygen atom in conformation B with the axial hydrogen at its rear; this adverse interaction might increase the stretching force constant and increase the absorption frequency.

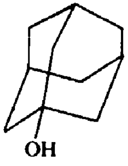
---

* Dalton *et al.*[7] made no mention of the asymmetrical OH absorptions of **6** and **7**, which we observed. Apparently, the study of Dalton *et al.* did not report "slightly asymmetrical" absorptions. Also according to these authors, 5α-cholestan-3β-ol had a symmetrical OH band, whereas this study and that of Aaron and Rader[13] found an asymmetrical OH absorption for this alcohol.

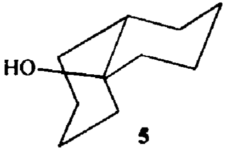
TABLE 3. ASSIGNMENTS OF C—O ROTAMERS TO COMPONENT O—H STRETCHING ABSORPTIONS

Compound	α/β[a]	No. of Rotamers	Rotamer[b] Type	ν max (cm^{-1})	Band Width[c] (cm^{-1})	Relative[d] Absorbance
1. 5α-Cholestan-5α-ol[7]		2	D	3629	20	1·0
		1	C	3611	18	1·9
2. *trans*-9-Decalol	0·5	2	D	3625	14	1·0
		1	C	3613	14	1·3
3. 1-Adamantanol	1·0	3	C	3605	14	
4. 1-Hydroxybicyclo[2.2.2]octane	1·0	3	C	3608	14	
5. *cis*-9-Decalol	1·4	1	D	3621	16	1·0
		2	C	3608	13	1·5
6. *trans*-4-t-Butyl-1-methylcyclohexanol	1·4	1	D	3621	12	1·0
		2	C	3613	13	1·2
7. *cis*-4-t-Butyl-1-methylcyclohexanol	1·2	3	C	3611 (3611)[7]	14 (16)[9]	—
8. 5α-Cholestan-3β-ol	0·67 (0·57)[13]	1	C	3614	13	1·1
		2	B	3623	13	1·0
9. Cholesterol	0·54 (0·64)[13]	1	C	3614 (3613)[e]	14 (18)[e]	0·9 (0·6)[e]
		2	B	3623 (3623)[e]	13 (16)[e]	1·0 (1·0)[e]
10. *trans*-4-t-Butylcyclohexanol	0·61 (0·64)[13]	1	C	3614	14	1·0
		2	B	3624	14	1·0
11. *cis*-4-t-Butylcyclohexanol	0·90 (0·94)[13]	2	B			
		1	D	3626 (3629)[13]	16 (17)[13]	
12. 5α-Cholestan-3α-ol	1·0 (0·98)[13]	2	B			
		1	D	3625 (3625)[7] (3627)[13]	16 (17)[7] (15)[13]	
13. 2,2-Dimethyl-*trans*-6-methyl-cyclohexanol	[f]	1	E	3614	16	0·6
		2	F	3639	15	1·0
14. 2,2-Dimethyl-*cis*-6-methylcyclohexanol	0·7	1	D	3624	18	0·3
		2	F	3644	16	1·0
15. 2,2,6,6-Tetramethylcyclohexanol[h]	0·8	1	D	3624	13	0·5
		2	F	3642	14	1·0

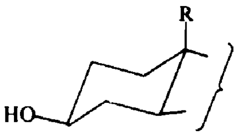
16. 2,2-Dimethyl-*trans*-4-t-butylcyclohexanol[g]	0·5	1	F	3632	11	1·0
		1	E			
		1	B	3622	17	0·7
17. 2,2-Dimethyl-*cis*-4-t-butylcyclohexanol	0·6	1	D	3625	14	0·2
		1	B			
		1	F	3636	14	1·0



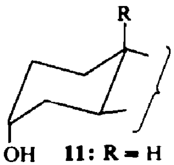
3



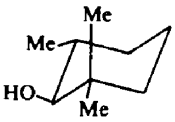
5



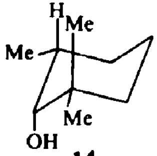
8,9: R = CH_3
10: R = H



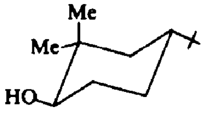
11: R = H
12: R = Me



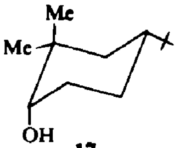
13



14



16



17

---

[a] See footnote *a* of Table 1.

[b] See Chart II for a structural description of rotamer types.

[c] Measured at half the maximum absorbance.

[d] Statistically corrected for the presence of two equivalent rotamers.

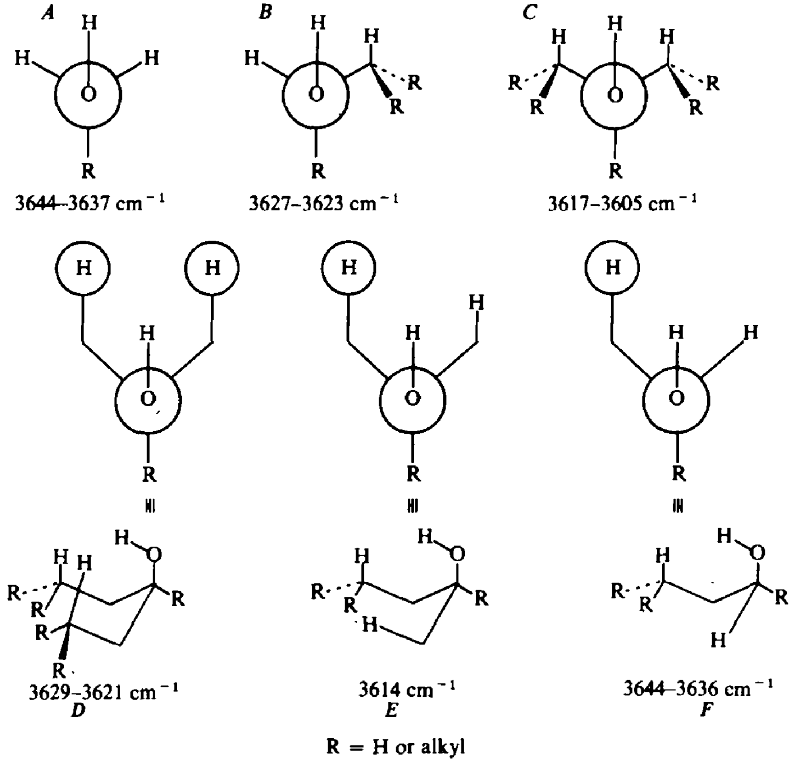
[e] M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan* **32**, 306 (1959) decomposed the OH spectrum of cholesterol into two bands but did not assign these component bands to C—O rotamers.

[f] A resolved doublet OH absorption was observed.

[g] Assignments of component OH bands to rotamers were not made (see text).

[h] The same types of C—O rotamers are present for both OH (eq) and OH (ax) conformations.

Chart II. Rotamer types and their assigned OH stretching frequencies.



Aaron and Rader[13] suggested that axial alcohols gave symmetrical spectra because only one type of rotamer (B and not D) was present (Chart II). They did not consider the alternative explanation which we favor: that both B and D type rotamers are present in substantial amounts, but both give absorptions at about the same position.

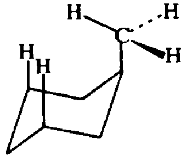
In the tertiary alcohols just considered, D type rotamers were assigned to bands at 3625 cm^{-1} (**2**), 3621 cm^{-1} (**5** and **6**) and at 3629 cm^{-1} (**1**) (Table 3). In acyclic alcohols (Table 2), B type rotamers are expected to absorb in the same region, at 3627 cm^{-1} B rotamers are also present in equatorial cyclohexanols; Table 3 lists examples at 3623 cm^{-1} (**8** and **9**) and at 3624 cm^{-1} (**10**). It seems clear from these examples that B and D type rotamers, which are the conformational types present in axial secondary cyclohexanols, should absorb at very nearly the same frequencies.

Because of the evidence that D type rotamers are present in the tertiary alcohols **1**, **2**, **5**, and **6**, we feel that they are very likely to be present in secondary axial cyclohexanols as well.

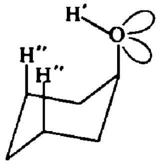
Based on the assumption that the extinction coefficients (ε's) of rotamer types B, C and D are all equivalent, the relative populations of these rotamer types in cyclohexanols without β substituents were estimated. Such estimations, although admittedly crude, should be reasonably accurate since the ε's for rotamers of saturated alcohols probably do not differ much; ε's of methanol (A type rotamer) and t-butanol

(C type rotamer) are about the same.[6] After statistical corrections are applied, the absorbances of rotamer types B and C in **8**, **9** and **10** are practically identical (Table 3), which suggests that these rotamers are of nearly equivalent energies. As compared with a D type rotamer, a C type rotamer appears to be about 20–90% more populated (cf. statistically corrected rotamer absorbances of **1**, **2**, **5** and **6** in Table 3). A B type rotamer probably is also 20–90% more populated than a D type rotamer. If this is the case, then in secondary axial cyclohexanols there should be about 20–30% of D type rotamer and about 70–80% of B type rotamers.

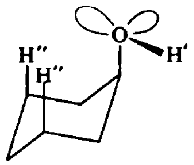
The enthalpy difference of about 2 kcal/mole[31] between the axial and equatorial conformers of methylcyclohexane has been attributed to *gauche* interactions between



an axial methyl group and the C_3 and C_5 methylene groups.[32] Part of the 2 kcal/mole difference is caused by steric repulsion of the 3,5-diaxial hydrogens and a *syn* hydrogen of an axial methyl group. Rotamer D, where the OH hydrogen can presumably interact analogously with the 3,5-diaxial hydrogens, seems to be only 0·1–0·4 kcal/mole less stable than rotamer B, in which such a repulsive interaction is absent.



D



B

A possible explanation for this small energy difference is that rotamer B is destabilized by an interaction between a lone pair of electrons on oxygen and the 3,5-diaxial hydrogens, which is almost as great as the H′:H″ repulsive interactions in rotamer D. In other words, an oxygen lone pair of electrons is only slightly "smaller" than an H atom.

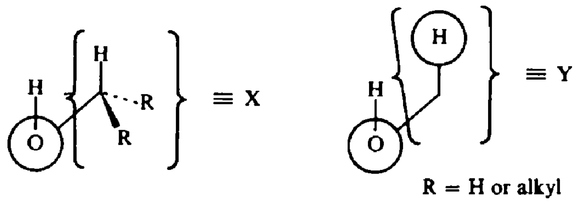
Recently Allinger *et al.*[33] have pointed out that other effects can largely account for behavior previously ascribed to the "size" of lone pairs of electrons. Our results perhaps also can be explained without considering the lone pairs of electrons. Nonbonded interactions between atoms in a system are either attractive or repulsive. It is entirely possible that the H:H repulsions present in rotamer D are compensated to some extent by attraction of the OH hydrogen with some of the ring atoms. When the OH hydrogen points away from the ring as it does in rotamer B, there will be fewer repulsions, but also fewer attractions. Alternatively, distortions from a "regular" geometry might permit a reduction in the energy difference between rotamers B and D.

Secondary equatorial alcohols in the cyclohexane series, provided there are no α-substituents, have two equivalent B type rotamers and one C type rotamer. Both of these rotamer types should give rise to bands at different frequencies. For this reason such alcohols should display asymmetrical spectra[13] and lower average absorption positions.[30]

Additional rotamer types E and F (Chart II) can be generated by β-Me substitution, as in the *trans* **13** and *cis* **14** isomers of 2,2,6-trimethylcyclohexanol, 2,2,6,6-tetramethylcyclohexanol (**15**) and *trans* **16** and *cis* **17** 2,2-dimethyl-4-t-butylcyclohexanol. Details of the analysis of these compounds may be found in Table 3.

Three rotamer types are present in **16** and **17**. However, the OH absorption of **17** should be composed of two components, since B and D type rotamers absorb at about the same frequency. On the other hand, B, E and F type rotamers present in **16** would be expected to have different absorption frequencies (Chart II); consequently, the OH absorption should be composed of three components. The problem of deciding how many component bands are found in an asymmetrical peak is complicated by the fact that even a symmetrical band can be decomposed artificially into any number of symmetrical components. We have adopted the conservative policy of decomposing each experimental spectrum into the minimum number of symmetrical bands. For the alcohols listed in Table 3, decomposition of the OH absorptions into *two* components produced good agreement between the calculated and experimental spectra. If three component bands were assumed, spectral decomposition did not produce a unique solution as there are several ways to decompose these relatively narrow absorptions into three components. The OH spectrum of **16** could have been decomposed into three bands with maxima at positions about those expected on the basis of rotamer types, but these results would not necessarily be meaningful. In view of this problem, no rotamer assignments were made for **16**.

The agreement between the frequencies of rotamers of the same type in Table 3 provides additional support to the postulation by Ōki and Iwamura[6] that only the local environment of the OH group determines its stretching frequency. Furthermore, a substituent *gauche* to the OH proton appears to produce a characteristic and generally constant effect on the OH stretching frequency. To simplify discussion of this point, substituents on the carbon bearing the OH will be designated as either X, Y or H. For example, the substituents influencing the OH group in rotamer E (Chart II) are X and Y. Substituents X and Y reduce the rotamer absorption frequencies relative to hydrogen by about 15 cm^{-1} and 8 cm^{-1}, respectively (Table 4). By using these substituent effects and rotamer type A as a reference, OH frequencies were calculated for the other cases. The general good agreement in Table 4 between the calculated frequencies and the experimental ones illustrates the constancy of the substituent effects.



Acyclic alcohols. In their pioneering paper on conformational heterogeneity, Ōki and Iwamura[6] presented spectral data for many acyclic saturated alcohols—data not listed earlier in Table 1 are given in Table 5. They proposed that each of the C—O rotamers of these alcohols belongs to either of three general types (A, III and IV),

TABLE 4. COMPARISON OF EXPERIMENTAL OH STRETCHING FREQUENCIES WITH THOSE CALCULATED ON THE BASIS OF THE *gauche* SUBSTITUENTS

Rotamer type	Substituents[a]	Exper[b] ν_{max} (cm^{-1})	Calc[c] ν_{max} (cm^{-1})
A	2 H	3640	(3640)
B	H, X	3625	3625
C	2 X	3611	3610
D	2 Y	3624	3624
E	X, Y	3614	3617
F	H, Y	3639	3632

[a] Substituents *gauche* to the OH hydrogen.

[b] Average of the observed rotamer OH stretching frequencies presented in Table 3.

[c] Type A rotamer was the reference. Substituent effects on the rotamer OH stretching frequencies were taken as: H = 0 cm^{-1}; X = -15 cm^{-1}; $Y = -8$ cm^{-1}.

TABLE 5. C—O ROTAMERS AND O—H STRETCHING ABSORPTIONS OF ACYCLIC SATURATED ALCOHOLS

	R	C—O Rotamers[a]	Estimated[b] ν_{max} (cm^{-1})	Spectral data ν_{max} (cm^{-1})[e] Band 1	Band 2	A1/A2[c, d]
			Primary Alcohols [RCH_2OH]			
18.	Et	(A, 2B), 2(A, B, F)	3640 3625	3637	3627	1·8
19.	Me_2CH	2(A, B, F), (A, 2F)	3640 3625	3640	3626	2·6
20.	Me_3C	(A, 2F)	3639	(3640)[c]		
				3642	3632	6·0
			Secondary Alcohols [$R(CH_3)CHOH$]			
21.	Et	(2B, F), (2B, C), (2B, E)	3639 3625 3613	3619	3615	3·3
22.	Me_2CH	(C, B, F), (B, E, F), (A, B, E)	3639 3625 3613	3632	3618	2·5
23.	Me_3C	(B, E, F)	3639 3625 3614	3636	3621	2·1
			Tertiary Alcohols [$R(CH_3)_2COH$]			
24.	Et	2(2C, E), (3C)	3612	3617		

[a] The C—O rotamers of each distinct C—C rotamer are enclosed in parentheses. The various C—C rotamers are listed from left to right in an assumed order of decreasing stabilities. We have assumed that the energies of *gauche* interactions are in the following order: Me · · Me > Me · · OH > Me · · H > H · · OH.

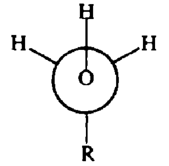
[b] The rotamer absorption frequencies used for our analysis are listed in Table 4. The superposition of two rotamer absorptions which usually differ in frequency by less than 5 cm^{-1} was assumed to produce a nearly symmetrical summation band.

[c] Taken from Ref. 6.

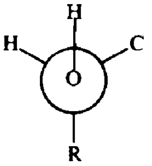
[d] (Area of band 1)/(area of band 2).

[e] This study.

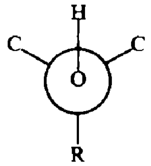
A



III



IV



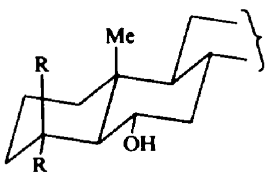
and furthermore that rotamers of the same type all have similar absorption frequencies. What these investigators failed to consider was that various substituents on the carbon atoms *gauche* to the OH bond may influence the OH stretching frequency to different extents. For example, rotamer types B and F have significantly different absorption frequencies (about 3625 cm^{-1} and about 3639 cm^{-1}, respectively) even though according to the previous classification they are both type III rotamers. Ōki and Iwamura did not make the necessary distinctions between B and F type rotamers and between C, D and E type rotamers; therefore, a re-evaluation of their spectra data was undertaken.

We considered the C—O rotamers present and assigned to them the characteristic absorption frequencies shown in Chart II. The details are presented in Table 5. By this procedure the number of component bands and their peak positions were estimated. The agreement between the estimated peak positions and those either calculated or observed directly is generally quite good for primary and tertiary alcohols. The spectral data of neopentyl alcohol (**20**) might at first appear to be an exception since we would expect an OH band at about 3639 cm^{-1}, which would be symmetrical or nearly so (rotamer types A and F have similar absorption frequencies), whereas the previous investigators reported two component bands. Yet, in fact, the OH spectrum undoubtedly observed by Ōki and Iwamura supports our expectation. Addition of the calculated components indicates that the OH absorption which they found was very nearly symmetrical; the minor band is only 15% as large as the major one and the separation between the peaks is only 10 cm^{-1}. The 3632 cm^{-1} band seems too weak to be a rotamer absorption (both A and F type rotamers normally have strong absorptions) and also is not found in the frequency ranges associated with A and F type rotamers (Chart II). Upon re-examination of the spectrum of **20**, we observed a practically completely symmetrical OH band at 3640 cm^{-1}, which is in striking agreement with our analysis.

According to our expectations, the spectra of **21–23** should be a composite of at least three component bands. Because these spectra were decomposed into only two bands by Ōki and Iwamura, the accuracy of our estimations could not be readily judged.

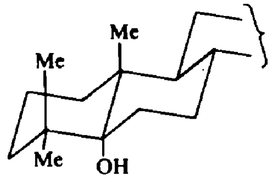
After the draft of our study was completed, a paper by Fétizon, Golfier and Rens[34] appeared in which the OH spectra of certain saturated steroidal alcohols were reproduced and discussed. Of particular interest to us were the spectra of three types of cyclohexanols (**25–27**), which we had not investigated. These examples provided further tests of our ability to rationalize OH spectra on the basis of the C—O rotamers present.

Fétizon *et al.* assigned the major absorption band of **25** at 3635 cm^{-1} to rotamer C which was presumed to be less hindered, and the minor absorption band at 3609 cm^{-1} to rotamers F and B. These assignments are inconsistent with our previous deter-



25: R = H, $\nu_{OH} = 3635\ cm^{-1}, 3609\ cm^{-1}$

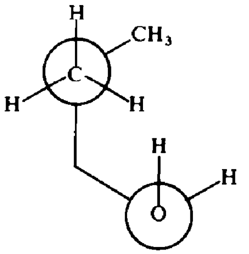
26: R = Me, $\nu_{OH} = 3616\ cm^{-1}, 3650\ cm^{-1}$ (sh)



27 $\nu_{OH} = 3637\ cm^{-1}$

minations of rotamer absorption frequencies. By contrast, the following assignments quite satisfactorily account for the observed spectrum. The 3635 cm^{-1} band results instead from a relatively intense F type rotamer absorption. In the reproduced spectrum, there definitely appears to be a third band located between the two maxima. This submerged band we attribute to a B type rotamer, which normally absorbs at about 3625 cm^{-1}. The maxima at 3609 cm^{-1} is then assigned to a C type rotamer.

The major asymmetrical band at 3616 cm^{-1} in the spectrum of **26** most likely is a composite of the absorptions of rotamer types B and C. Fétizon *et al.* suggested that the remaining rotamer, type H, may be responsible for the weak absorption near 3650 cm^{-1}. An H type rotamer appears to be sterically unfavorable and consequently a relatively low absorption intensity for this rotamer seems reasonable.



H type rotamer

In **27** two D type rotamers and one E type rotamer are present. On the basis of these rotamers, a major OH band near 3625 cm^{-1} and a minor one near 3614 cm^{-1} initially might have been expected. Contrary to these expectations, an asymmetrical singlet OH absorption at 3637 cm^{-1} was actually observed. This is the only example where the OH spectrum appears inconsistent with the rotamers present.

The A ring of **27** should be considerably flatter than normal in order to partially relieve the repulsive interaction between the *syn* diaxial methyl groups.* Such ring flattening brings a 4-methyl group closer to the OH group and increases the distance between the OH group and axial hydrogens in the A ring. As a result, the geometries of one of the D rotamers and an E type rotamer should be different from those in the other alcohols investigated. Perhaps this is the explanation for the anomalous OH absorption of **27**.

Our general success in assigning the OH spectral component bands of a relatively limited series of cyclic alcohols to the C—O rotamers present indicates that the OH spectra of other saturated alcohols might be similarly analyzed. Except for alcohols

---

* One *syn*-diaxial methyl–methyl interaction is not sufficient to convert a cyclohexane ring from the usual chair form to a boat form (Ref. 32, p. 470).

closely analogous to those discussed here, i.e. compounds with hydroxyl groups substituted on undistorted cyclohexane rings, considerable caution should be exercised when predicting OH spectra from data given in this study—especially since the factors responsible for the characteristic rotamer absorption frequencies have not yet been elucidated. **Note added in proof*: Dr. J. Sicher and Dr. M. Tichy have informed us of work by A. Vitek on conformationally fixed 2-methylcyclohexanols. While the rotamer band *positions* observed are in agreement with our assignments, detailed analysis shows that the *intensities* of certain rotamers are significantly greater than those of others. Further study is planned.

EXPERIMENTAL

IR spectroscopic techniques. All IR spectra were determined on a Perkin–Elmer 421 double beam grating spectrometer. Reagent grade CCl_4 was dried over P_2O_5, decanted and used without further purification. 10 mm cells of IR silica were used. Concentrations of the alcohols were 1 mg/ml of CCl_4 or lower to prevent intermolecular association. The calibration of the instrument was checked daily against atmospheric water vapor; frequencies were so corrected. Excellent reproducibility was observed.

Sources of compounds. Ethanol, 2-propanol, methanol, t-butanol, **8**, **9** and **20** are commercially available and were distilled or recrystallized before use. We are indebted to Professor G. Hamilton who kindly supplied samples of **2**[35] and **5**[35], to Dr. W. J. A. VandenHeuvel[36] for **12**, to Dr. R. C. Fort, Jr.,[37] for **3**, to Dr. R. Gleiter who provided **4**, **6**[38] and **7**,[38] to Drs. P. Laszlo and S. Bory for **13–15**[39] and to Dr. E. L. Eliel[40] for **16** and **17**.

trans-4-t-*Butylcyclohexanol* (**10**) *and* cis-4-t-*butylcyclohexanol* (**11**). Commercial 4-t-butylcyclohexanol (Matheson) consisting of 73% of **10** and 27% of **11** was fractionally distilled. A fraction containing 85% of **11** was separated by "dry-column" chromatography.[41] Alumina (Fisher No. A-540) deactivated by shaking with 8% by weight of water was the adsorbent and $CHCl_3$ was the eluent. After the eluent had reached the bottom of the column, the column was divided into 6 portions, each of which was subsequently extracted with ether. Following the evaporation of solvent, the crystals obtained from each fraction were tested for purity by GLC. Since **11** is less strongly adsorbed on an alumina column,[42] crystals obtained from the lower portions of the column were pure **11**. A distillation cut containing 95% of **10** was similarly separated by "dry-column" chromatography to yield pure **10**.

Acknowledgements—We would like to thank the Whitehall Foundation who provided funds for the infrared spectrometer used in this study. Computer time was kindly provided by the Princeton University computer centre, supported in part by National Science Foundation Grant GP-579. This research was supported, in part, by the National Institutes of Health, Grant No. A107766, and the Petroleum Research Fund, administered by the American Chemical Society.

REFERENCES

[1] Review: M. Tichý, *Advances in Organic Chemistry: Methods and Results*, (Edited by R. A. Raphael, E. C. Taylor and H. Wynberg), Vol. 5; p. 115. Wiley (1965).

[2] R. M. Badger and S. H. Bauer, *J. Chem. Phys.* **4**, 711 (1936).

[3] P. Tuomikoski, *Suomen Kemistilehti* **23B**, 44 (1950);
P. Tuomikoski, E. Pulkkinen, P. Hirsjärvi and N. J. Toivonen, *Ibid.* **23B**, 53 (1950).

[4] T. D. Flynn, R. L. Werner and B. M. Graham, *Austral J. Chem.* **12**, 575 (1959).

[5] R. Piccolini and S. Winstein, *Tetrahedron Letters* No. 13, 4 (1959).

[6] M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan* **32**, 950 (1959).

[7] F. Dalton, G. D. Meakins, J. H. Robinson and W. Zaharia, *J. Chem. Soc.* 1566 (1962).

[8] J. Fruwert, G. Hanschmann and G. Geiseler, *Z. Physik Chem.* **228**, 277 (1965).

[9] P. Arnaud and Y. Armand, *C.R. Acad. Sci., Paris*, **255**, 1718 (1962);
Y. Armand and P. Arnaud, *Ann. Chim.* **9**, 433 (1964).

[10] M. Boyer and M. M. Claudon, *Bull. Soc. Chim. Fr*, 1139 (1966).

[11] P. J. Krueger and H. D. Mettee, *Canad. J. Chem.* **42**, 347 (1964).

[12] E. L. Saier, L. R. Cousins and M. R. Basila, *J. Chem. Phys.* **41**, 40 (1964).

[13] H. S. Aaron and C. P. Rader, *J. Am. Chem. Soc.* **85**, 3046 (1963);
H. S. Aaron, C. P. Ferguson and C. P. Rader, *Ibid.* **89**, 1431 (1967).

[14] P. von R. Schleyer, D. S. Trifan and R. Bacskai, *Ibid.* **80**, 6691 (1958).

[15] M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan* **32**, 567 (1959).

[16] M. Ōki and H. Iwamura, *Ibid.* **32**, 955 (1959).

[17] M. Ōki and H. Iwamura, *Ibid.* **35**, 1552 (1962).

[18] L. Joris, P. von R. Schleyer and R. Gleiter, *J. Am. Chem. Soc.* **90**, 327 (1968).

[19] J. D. Swalen, *J. Chem. Phys.* **23**, 1739 (1955) and Refs therein cited.

[20] G. M. Barrow, *Ibid.* **20**, 1739 (1952).

[21] E. V. Ivash and D. M. Dennison, *Ibid.* **21**, 1804 (1953).

[22] This study.

[23] A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.* **85**, 1715 (1963); see G. A. Sim, *Ann. Rev. Phys. Chem.* **18**, 67 (1967).

[24] A. B. Foster, A. H. Haines and M. Stacey, *Tetrahedron* **16**, 177 (1961).

[25] H. Mori, S. Ōmura, N. Kobayashi and Y. Tsuzuki, *Bull Chem. Soc. Japan* **38**, 2149 (1965), and previous publications;
S. Wada, *Ibid.* **35**, 707 (1962);
R. Piccolini, Ph.D. Thesis, UCLA, 1959; cf, Ref. 5.

[26] See R. H. Müller, *Analyt. Chem.* **38**, No. 12, 121A (1966), and *Chem. Eng. News* **43**, 50 (Nov. 15, 1965).

[27] [a] H. Stone, *J. Opt. Soc. Am.* **52**, 998 (1962);
[b] D. Papousek and J. Pliva, *Collection Czech. Chem. Commun.* **30**, 3007 (1965);
[c] J. Pitha and R. N. Jones, *Canad. J. Chem.* **44**, 3031 (1966).

[28] D. A. Ramsay, *J. Am. Chem. Soc.* **74**, 72 (1952).

[29] L. Joris, Ph.D. Thesis, Princeton University, 1968.

[30] A. R. H. Cole, G. T. A. Müller, D. W. Thornton and R. L. S. Willix, *J. Chem. Soc.* 1218 (1959).

[31] E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Res. Natl. Bur. Std.* **39**, 173 (1947);
C. W. Beckett, K. S. Pitzer and R. Spitzer, *J. Am. Chem. Soc.* **69**, 2488 (1947).

[32] E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* p. 43. Interscience, New York (1965).

[33] N. L. Allinger, J. A. Hirsch and M. A. Miller, *Tetrahedron Letters* No. 38, 3729 (1967).

[34] M. Fétizon, M. Golfier and J. Rens, *Bull. Soc. Chim. Fr*, 2680 (1967).

[35] Prepared according to the procedure of W. Hückel, D. Maucher, O. Fechtig, J. Kurz, M. Heinzel and A. Hubele, *Liebigs Ann.* **645**, 115 (1961).

[36] W. J. A. VandenHeuvel, R. N. Stillwell, W. L. Gardiner, S. Wikstrom and E. C. Horning, *J. Chromatog.* **19**, 22 (1965).

[37] R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.* **30**, 789 (1965).

[38] Prepared according to the procedure of C. H. DePuy and R. W. King, *J. Am. Chem. Soc.* **83**, 2743 (1961).

[39] Prepared according to the procedure of G. Barraud, R. Cornubert and A. M. Lemoine-Tressont, *Bull. Soc. Chim. Fr*, 1499 (1957).

[40] E. L. Eliel, S. H. Schroeter, T. L. Brett, F. J. Biros and J.-C. Richer, *J. Am. Chem. Soc.* **88**, 3327 (1966).

[41] For a description of the method, see B. Loev and K. M. Snader, *Chem. & Ind.* 15 (1965).

[42] S. Winstein and M. Holness, *J. Am. Chem. Soc.* **77**, 5562 (1955).