NOTES

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Intramolecular Hydrogen Bonds. XVI.[1] Preferable Conformation of 1-Tetralols

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It has recently been suggested[2,3] that, for the OH–π interaction in 1-tetralols, the *quasi-equatorial* conformation of the hydroxyl group is preferable to the *quasi-axial* one. This seems contradictory if the hydrogen-accepting site is the π-electrons on the 9-position as in benzyl alcohols,[4] because examination of the model shows that the *quasi-axial* conformation is sterically preferable for the interaction. In order to solve this problem, the steric and electronic effects of substituents on the infrared OH spectra of 1-tetralols have been investigated in their dilute carbon tetrachloride solutions.

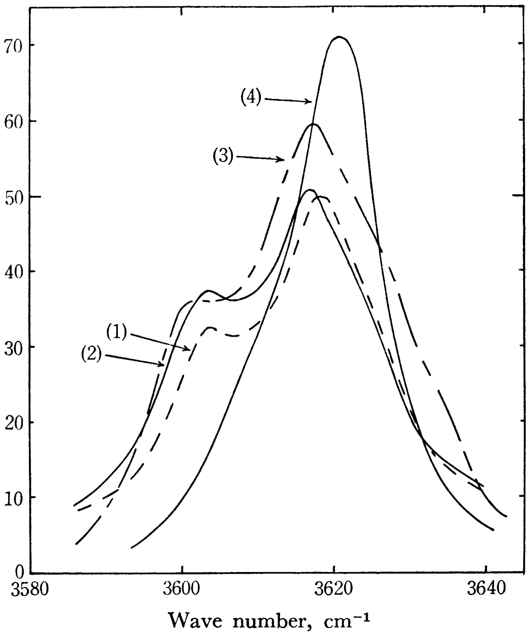

Fig. 1. OH Spectra of 1-tetralols: unsubst. (1), 7-methoxy (2), 7-nitro (3), and 5,8-dimethyl (4).

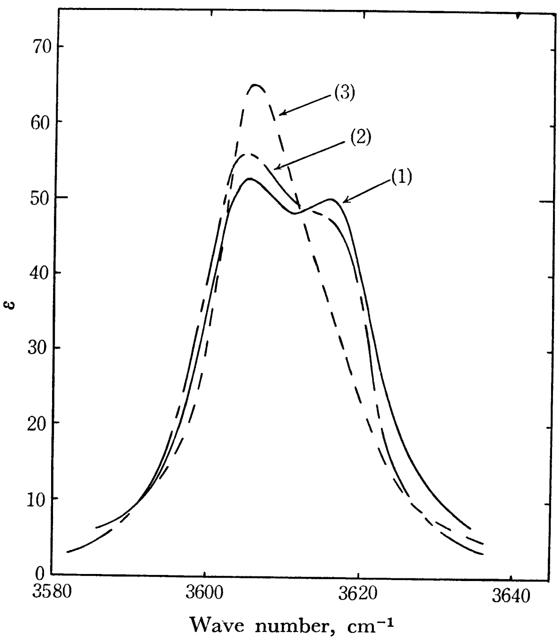

Fig. 2. OH Spectra of 1-tetralols: 1-methyl (1), 1-methyl-7-methoxy (2), and 1,5,8-trimethyl (3).

The OH spectra of 1-tetralols and 1-methyl-1-tetralols, which consist of two split bands, are in contrast with each other (Figs. 1 and 2). In the former the higher-frequency band is stronger, while in the latter the lower-frequency band is stronger, and the weaker bands of both spectra almost disappear by the 8-methyl substitution. The following can be considered as reasons for band splitting: (1) interaction between the OH group and the π-electrons,[4,5] (2) rotational isomerism of the OH group about the C–O bond,[4,5] and (3) conformational isomerism of the OH group to be caused by the ring conversion of the saturated-ring portion. The observed spectra should be contributed by different OH species. However, the pronounced spectral change by the 8-methyl substituent can be explained mainly by (3), *viz.*, by the conformational interconversion of the saturated-ring portion resulting from the steric interaction between the *quasi-equatorial* 1- and the 8-substituents, because the 8-substituent is not expected to have a similarly significant influence on (1) and (2). It thus appears that the steric repulsion between the *quasi-equatorial* 1- and the 8-substituents is sufficiently high to overcome the steric interaction between the *quasi-axial* 1-substituent and the *axial* 3-hydrogen atom.[6] Therefore, the hydroxyl groups in 1-tetralols are preferably in a *quasi-axial* conformation, while in 1-methyl-1-tetralols they are in a *quasi-equatorial* conformation, as can be expected from the oridnary order of steric size: $H < OH < CH_3$.

The higher- and the lower-frequency bands can thus be assigned to the *quasi-axial* and *-equatorial* OH groups,

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[1] Part XV; N. Mori, Y. Asabe, J. Tatsumi, and Y. Tsuzuki, This Bulletin, **43**, 3227 (1970).

[2] K. Hanaya, *Nippon Kagaku Zasshi*, **90**, 314 (1969).

[3] K. Hanaya, *ibid.*, **91**, 82 (1970).

[4] M. Ōki and H. Iwamura, This Bulletin, **32**, 955 (1959); **35**, 1552 (1962).

[5] M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

[6] A similar effect of steric interaction is recognized in several 1-substituted cyclohex-2-enes.[3,7]

[7] E. W. Garblish, Jr., *J. Org. Chem.*, **27**, 4249 (1962).

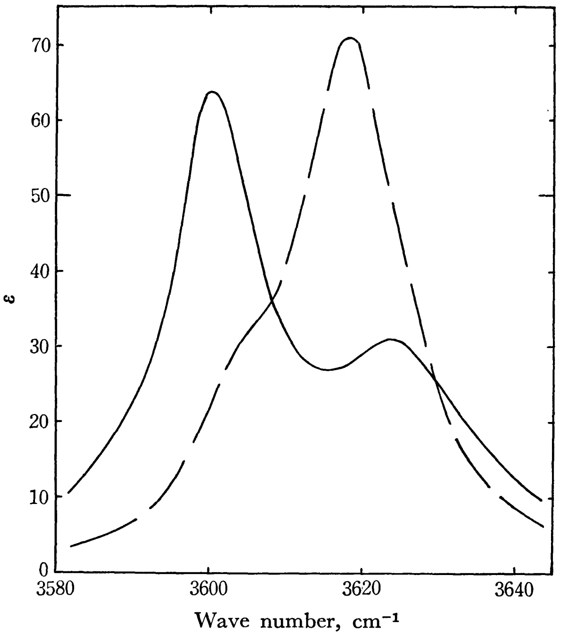

Fig. 3. OH Spectra of *cis*- and *trans*-3-phenyl-1-tetralols: *cis* (——), *trans* (– – –).

respectively. They probably contain further absorption bands due to the other OH species, such as their conformational and/or rotational isomers, to some extent.

In the interaction with the π-electrons, the observed effect of a 7-substituent on the intensity ratio indicates that one or both of the *quasi-axial* and *-equatorial* OH groups participate. The *quasi-equatorial* one evidently interacts, since the frequency is lower than both of the free ν_{OH} values (3627 and 3620 cm^{-1}) and the interacted ν_{OH} values (3616 and 3607 cm^{-1}) of α-phenylethanol and -isopropanol.[4] Substantially all the OH species in the *quasi-equatorial* conformation seem to interact, since 1,5,8-trimethyl-1-tetralol shows, apart from a very intense band of the *quasi-equatorial* interacted OH group, only a very low unsymmetry due to other OH species on the higher-frequency side.

Whether the *quasi-axial* OH group interacts is not clear on account of the fact that the OH frequencies of 1-tetralols are very close to the interacted OH frequency of α-phenylethanol, while those of 1-methyl-1-tetralols are close to the free OH frequency of α-phenylisopropanol. However, there are several suggestions for the *quasi-axial* OH group to be free; if it is assumed that *trans*-3-phenyl-1-tetralol is fixed in such a conformation that the hydroxyl and the phenyl group are *quasi-axial* and *equatorial*, respectively, the strong band observed at 3618 cm^{-1} should be assigned to the free OH species, with the unsymmetry of the band being attributable to the rotational isomerism about the C–O axis or the interacted OH species. The same assignment should be given for the unsymmetric band of 5,8-dimethyl-1-tetralol whose OH group should preferably be *quasi-axial.* If interaction take place, the *quasi-axial* OH group would be prone to an electronic effect of substituents. However, even the 7-nitro substitution results in no appearance of a significant band on the higher-frequency side, suggesting that the *quasi-axial* OH group is practically free, and the observed intensity ratio of the two bands (*quasi-axial* to *quasi-equatorial)* increases with the 7-substituents in the order: $CH_3O < H < NO_2$, suggesting that the electronic effect is operative on the *quasi-equatorial* OH group and the interaction between this group and the π-electrons becomes weaker in that order, thereby some of the interacted OH species becoming free and then *quasi-axial.* For the electronic effect of substituents, a further study of 5- and 6-substituted 1-tetralols would be desirable.

In the case of isomeric 3-phenyl-1-tetralols[8] (Fig. 3), the *trans* isomer may exist predominantly in a conformation with the *quasi-axial* OH group, as mentioned above. The *cis* isomer exists in two conformations; one con-

Table 1. Physical constants and apparent spectral data of 1-tetralols

Substituents in 1-tetralols	Mp (Bp) °C	ν_{OH}, cm^{-1}		
		*q.-ax.*OH (ε_a)	*q.-eq.*OH (ε_e)	$\varepsilon_a/\varepsilon_e$
Unsubstituted[9]	(126/12)	3618 (50)	3603 (32)	1.56
7-Methoxy[10]	38.2— 38.7	3616 (51)	3603 (37)	1.39
7-Nitro[11]	108 —108.5	3614 (60)	3601 (36)	1.67
5,8-Dimethyl[12]	92.0	3621 (65) 3610[a]		
1-Methyl[13]	88.5— 89.0	3616 (50)	3605 (53)	0.94
1-Methyl-7-methoxy	68 — 69	3616 (47)	3605 (56)	0.84
1,5,8-Trimethyl[14]	136	3615[a]	3606 (71)	
3-Phenyl (*cis*)[b]	99.5—100.5	3624 (31)	3600 (64)	0.46
(*trans*)[b]	98.5— 99.5	3618 (71) 3603[a]		

a) ν_{OH} at the shoulder part (the assignment is uncertain).

b) Configuration was determined by NMR spectroscopy.[15]

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[8] In the presence of a shoulder, the spectrum of the *trans* isomer differs somewhat from that reported by Hanaya,[2] probably because of the different temperatures of measurement (25°C in Hanaya's work, 20°C in our work).

[9] F. Strauss and L. Lemmel, *Ber.*, **54**, 25 (1921).

[10] D. G. Thomas and A. H. Nathan, *J. Amer. Chem. Soc.*, **70**, 331 (1948).

[11] Y. Asahina and T. Momose, *Yakugaku Zasshi*, **64**, 154 (1944).

[12] W. Cocker, B. E. Cross, J. T. Edward, D. S. Jenkinson, and J. McCormick, *J. Chem. Soc.*, **1953**, 2355.

[13] T. Kusama and D. Koike, *Nippon Kagaku Zasshi*, **72**, 683 (1951).

[14] E. D. Barnett and F. G. Sanders, *J. Chem. Soc.*, **1933**, 434.

tains the OH group in the *quasi-axial* conformation and the other, in the *quasi-equatorial* one. Preference of the latter indicates that the steric interaction between the *quasi-axial* 1-hydroxyl and the *axial* 3-phenyl group is higher than that between the *quasi-equatorial* 1-hydroxyl group and the 8-hydrogen atom. Accordingly, our spectral data support the configurations proposed by Mitsui *et al.* on the basis of NMR spectroscopy.[15]

Experimental

Samples. All the tetralols, except for 1-methyl-7-methoxy-1-tetralol, were prepared and purified by the methods described in the literature. Isomeric 3-phenyl-1-tetralols were further purified through chromatography on silica gel using a mixture of hexane and benzene. Their melting and/or boiling points were equal, or very close, to those reported. The above 7-methoxy-compound was prepared in the usual manner[13] from 7-methoxy-1-tetralone. (Found: C, 75.16; H, 8.50%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%).

Infrared Measurement. This was carried out at *ca.* 20°C in the same manner as described previously.[1] The concentration used was 0.003 mol/*l* in carbon tetrachloride and the cells used had a path-length of 5.0 cm.

The spectral data are summarized in Table 1 together with the physical constants.

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[15] S. Mitsui, A. Kasahara, and K. Hanaya, This Bulletin, **41**, 2526 (1968).