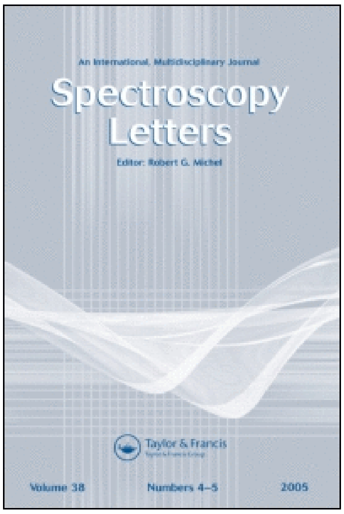

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INFRARED STUDIES OF HYDROGEN BONDING IN STERICALLY HINDERED HYDROXY COMPOUNDS

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Abstract

Hydrogen bonding in five benzhydrols and triphenyl methanol have been studied in the solid phase and on dissolution. Attempts have been made to characterize possible molecular species in the solid structure.

Introduction

The study of hydrogen bonding in a number of hydroxy compounds has been the subject of numerous investigations, many of them applying infrared spectroscopy. There have been very few studies however on the hydrogen bonding in the solid phase. In such cases, the orientation of the molecule is such as to form the strongest hydrogen bonds.[1] Although some novel work on the hydrogen bonds of solid alcohols[2-3], phenols[4] and formic acid[5] has been recently reported by Jakobsen and Brasch, most of the reported examples involve rather simple structures. It is thought that the hydrogen bonding studies in solids should be extended with more rigid systems[6-7] which may impose special constraints on the various stages of aggregation. The present paper describes formation of hydrogen bonds in five benzhydrols and triphenyl methanol in the solid phase and in CCl_4 solution. The motivation here was to try and gain an insight into the molecular species present in the solid compounds. The sterie hindering effect[8-9] as well as the electronic effect[10-11] of the branched substituents around the OH group may play a unique role in the process of hydrogen bond formation in these molecules.

Experimental

The following series of six branched hydroxy compounds were used in the study:

p,p^1-kelthane, o,p^1-kelthane, chlorfenethol, benzhydrol, 4,4^1-dichlorobenzhydrol and triphenyl methanol. With the exception of o,p^1-kelthane, all materials were commercially available and had been purified by recrystallization or thin layer chromatography. The o,p^1-kelthane obtained from NCI, was of EPA standard quality and no further purification was carried out.

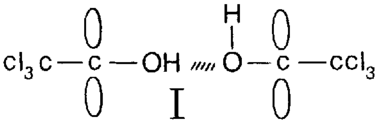
The infrared spectra of solid samples were examined in the OH fundamental stretching region using powdered KBr matrix techniques, and in some cases, as mull in nujol. The infrared spectrum of chlorfenethol was also recorded as a thin film obtained by rapid cooling of molten solid. Harshaw standard KBr was used and water absorption bands in a blank pellent were within 0.02 absorbance unit (Fig. I). Hydrogen bonding in solutions was examined in dry CCl_4 with a 1.0 mm cell.

All the spectra were run on a Perkin-Elmer 180 spectrophotometer. The accuracy in the measurement of frequencies listed in Table I was within 2 cm^{-1}. The temperature of air at the spectrometer was approximately 25.4^oC at all times.

Results and Discussions

Table I lists bonded and free OH frequencies for a number of branched hydroxy compounds in the solid phase and in CCl_4 solution while the spectra are shown in Figs. I-III.

It can be clearly seen (curves a and b of Fig. I) that the p,p^1-kelthane and the ortho isomer have three OH stretching absorptions, which vary very slightly in frequency or intensity from one isomeric form to another. Each band is characteristic of a given state of aggregation and the changes in the relative intensities of the three bands reflect the relative population of the three states of aggregation in the solid structure. In fact, there are essentially three reasonably distinct hydrogen bonded structures in the solid phase of the two compounds, as follows:



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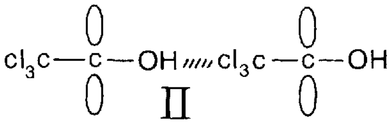

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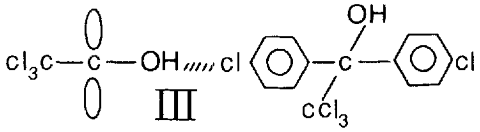
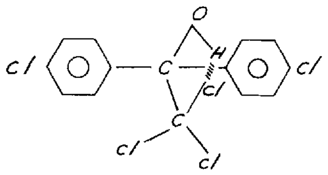


III



IV

Early studies[12,9] indicated that sterically hindered alcohols and phenols are less associated. The lowest frequency at 3528 cm^{-1} in p,p^1-kelthane and 3534 cm^{-1} of o,p^1-kelthane can be undoubtedly assigned to the structure I. Each of the isomers has a rigid structure and hydrogen bonding seems to be very weak. The phenyl rings are to be oriented in skew position[13] for the availability of the OH group for favorable bonding. The high-frequency component of p,p^1-kelthane at 3556 cm^{-1} may be due to either of the structures[14-15] II or III. It is rather difficult to differentiate the existence of the two bonded forms solely from infrared data. Although x-ray diffraction data could best solve the problem, unfortunately such crystallographic data are not yet available for these compounds. Still the absence of any band in this region in the spectrum of either chlorfenethol or 4,4^1-dichlorobenzhydrol (curves c, d and f of Fig. I) emphasizes the possibility of structure II over the structure III in the crystal.

Besides, the OH in these molecules seem to form intramolecular bonding with the Cl-atom of the CCl_3 group[16], (as shown in IV); this will probably give rise to a bonded OH frequency (OH ... Cl) near 3578 cm^{-1} Linke[17] reported the intramolecularly bonded OH frequency in cis o-chlorophenol and 2,4,6-trichloro phenol near 3547 cm^{-1}. The OH ... Cl angle will however make the intramolecular bridge weaker in the present molecules than would be the case if the angle were nearly straight. It is noteworthy that the free OH frequencies (ca 3575 cm^{-1}) in the solutions of the compounds in CCl_4 (Fig. III) are considerably lower than those of di-t-butyl-isopropyl carbinol[18] (3640 cm^{-1}) and di-tert-butylphenol[19] (3643 cm^{-1}). This could not be simply explained by the substituent effect of the electron-donating CCl_3 group. These arguments leave no doubt that the peak frequency near 3578 cm^{-1} is due to the OH stretching of intramolecularly bonded single molecule. Moreover, the presence of a band near 3575 cm^{-1} (curves a and b of Fig. I) conclusively suggests that p,p^1 and o,p^1-kelthanes contain small amounts of single molecules in the solid phase.

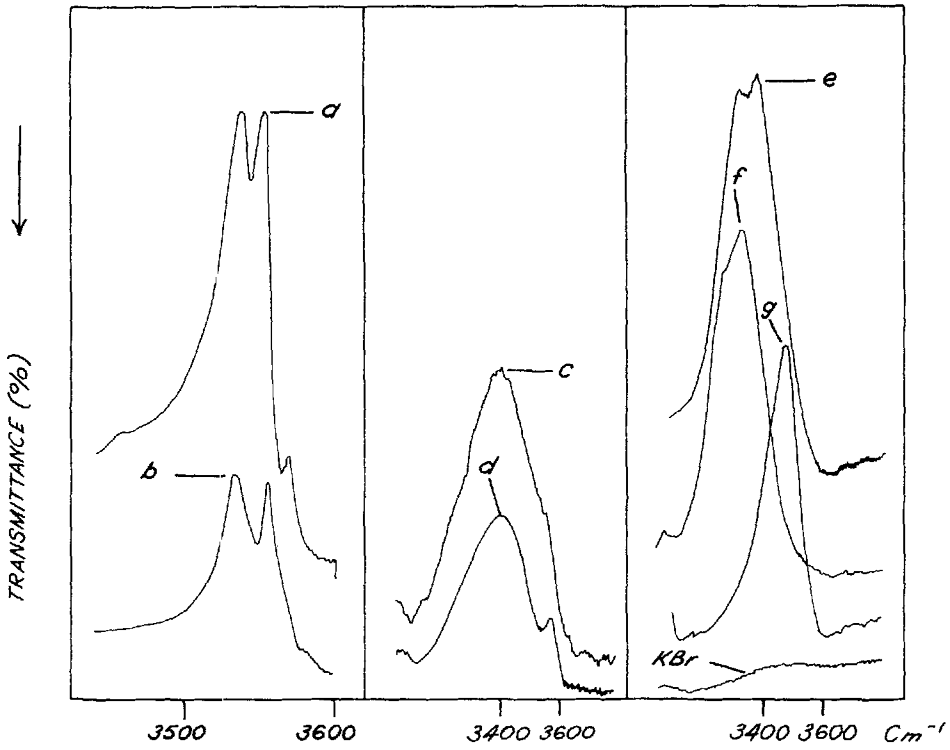


FIG. I. Hydrogen bonds in solids (a) p,p^1-kelthane, (b) o,p^1-kelthane, (c) chlorfenethol, (d) chlorfenethol (thin film after rapid cooling of molten solid), (e) benzhydrol, (f) 4,4^1-dichlorobenzhydrol, (g) triphenyl methanol.

Fig. II shows some pertinent spectral data for the two compounds as a mull in nujol. While p,p^1-kelthane is soluble in nujol, the intensity of the free hydroxyl absorption near 3575 cm^{-1} progressively increases with the gradual dilutions in nujol. Finally, at a stage of sufficient dilution (ca 6 drops/12 mg of sample) the free OH absorption predominates. On the otherhand, the intensity of free hydroxyl absorption in o,p^1-kelthane does not appreciably change in nujol, presumably because the sample is not sufficiently soluble in nujol. The absorption represented by the shoulder near 3530 cm^{-1} (curve b of Fig. III) in the spectrum of o,p^1-kelthane indicates significant population of bonded structure II even in the dilute

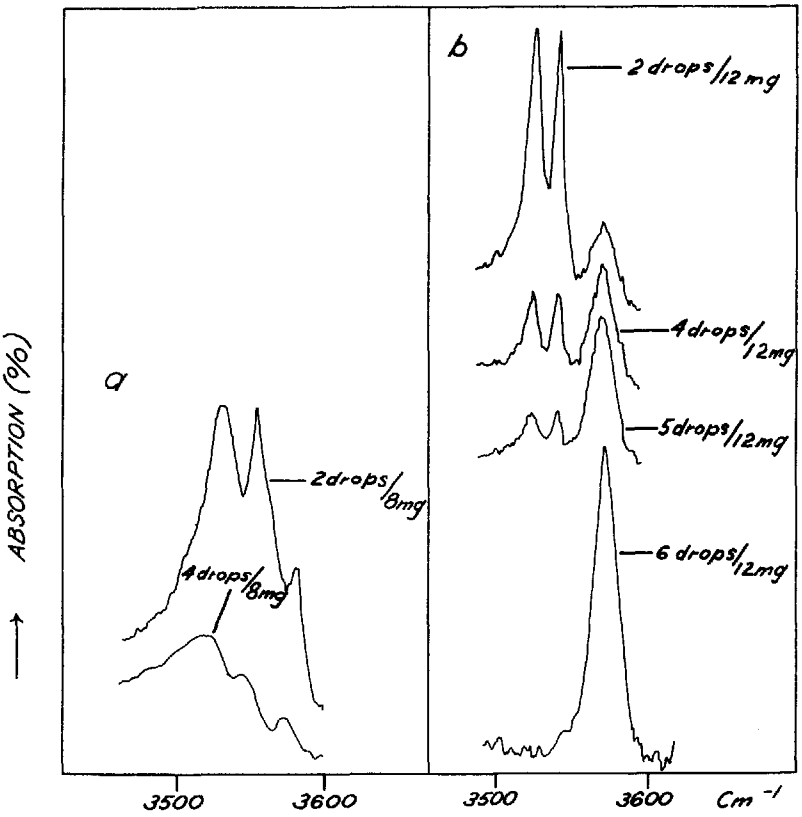


FIG. II. Infrared spectra in the ν(OH) region (mull in nujol) (a) o,p^1-kelthane, and (b) p,p^1-kelthane

CCl_4 solution. The corresponding band of p,p^1-kelthane does not however appear to resolve from the broad monomeric absorption.

In the spectrum of solid chlorfenethol (curves c and d of Fig. I), OH is clearly split into one broad component and one relatively sharp component, with the sharp component at higher frequency. Nearest-neighbor coupling^2 may be the underlying reason for the broadness of the polymeric OH absorption with the center at 3428 cm^{-1}. The presence of the band at 3575 cm^{-1} gives the spectrum of this compound quiet similar to those of p,p^1 and o,p^1-kelthanes. Certain proportion of free molecules in the bonded moiety has been suggested presumably because of crystal constrains[20].

The spectra of solid benzhydrol and 4,4^1-dichloro derivative show distinct features in the OH region (curve e and f of Fig. I). In each case, two components are obvious although the clear separation is not obtained in the latter compound. The lack of clear separation could result from the unknown effects of different crystal structures on hydrogen bonded structure. The double OH frequencies in these solid compounds may be due to coupling or crystal splitting. Falk and Whalley[21] and later, Jakobsen et al[2-3,22] observed similar behavior in their study of crystalline alcohols and their deuterated derivatives. No crystal splitting has however been observed in chlorfenethol presumably because of the stable glassy structure of the compound. Likewise, triphenyl methanol gives a relatively sharp single absorption in the (OH) region. It should be pointed out that the bonded OH in the solid compound (3472 cm^{-1}) is higher (+46 cm^{-1}) than that of chlorfenethol (curve g of Fig. I). This is explained by the fact that the -H ... O bond in solid chlorfenethol may be weaker than that in triphenyl methanol, as the frequencies usually increase with hydrogen-bond strength[23].

The dilution effect on OH frequencies are demonstrated in curves c-f of Fig. 3. The free OH frequencies have been assigned without difficulty as no other fundamental occurs in the region of the spectrum. Similarly, the absorption band at 3450-3480 cm^{-1} in the compounds has been clearly attributed to the bonded OH in the dimeric molecule and the assignment has been subsequently confirmed by the dilution studies[8,12]. The dimeric OH frequencies are however lower than those of sterically hindered alcohols[8] and phenols[19]. For example, o-t-bytyl phenol[19] shows dimeric

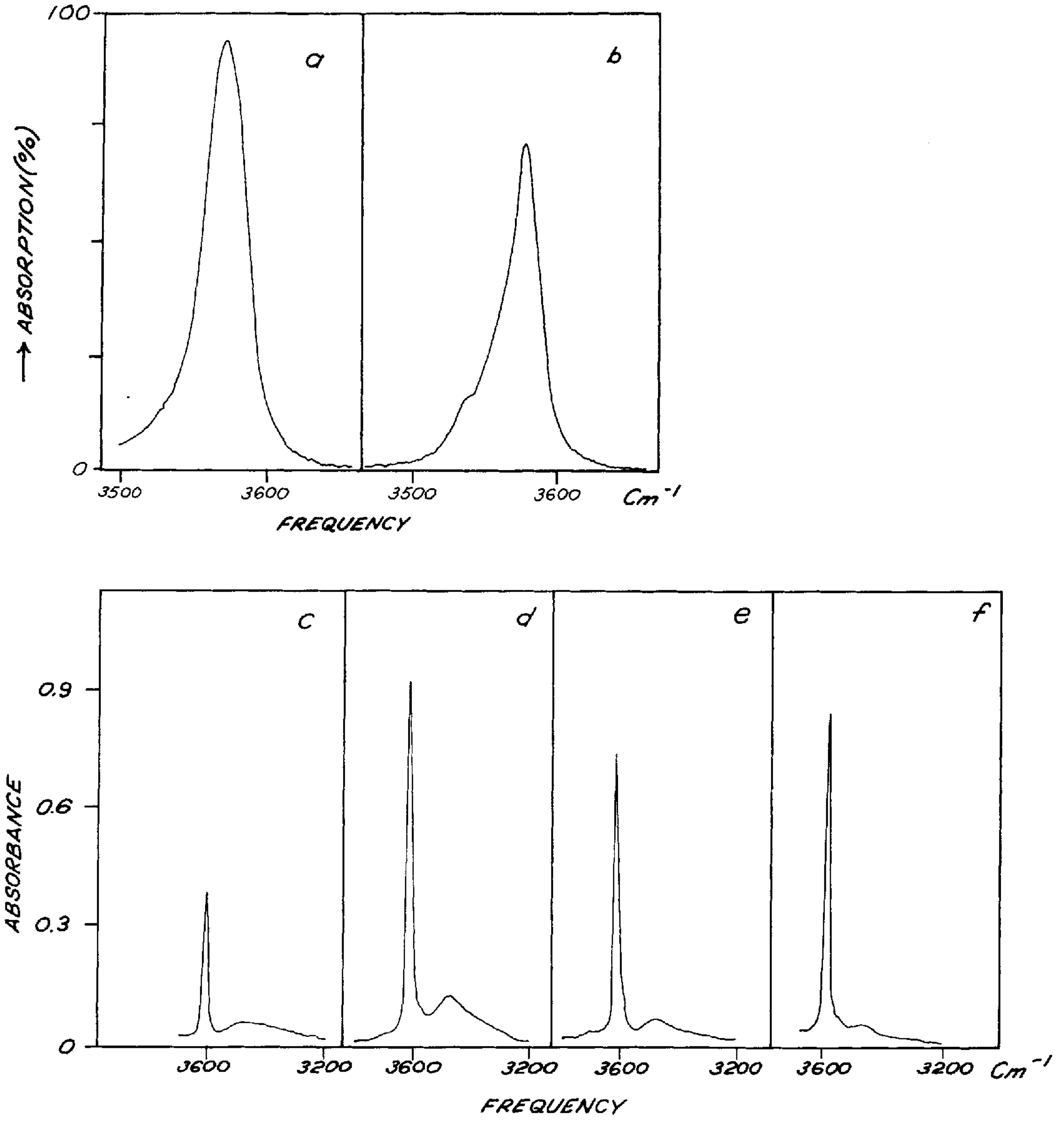


FIG. III. Infrared spectra in the ν(OH) region (CCl_4). Concentrations in moles per liter. (a) p,p^1-kelthane (0.0323), (b) o,p^1-kelthane (0.0413), (c) chlorfenethol (0.0481), (d) benzhydrol (0.1341), (e) 4,4^1-dichlorobenzhydrol (0.1183), and triphenyl methanol (0.0814).

TABLE I

OH Frequencies (cm^{-1}) in Benzhydrols and Triphenyl Methanol

COMPOUND	SOLID		MULL IN NUJOL		SOLUTION IN CCl_4	
	Free	Bonded	Free	Bonded	Free	Associated
p,p^1-Kelthane	3568	3528	3576	3528	3576	-
		3544		3544		
o,p^1-Kelthane	3578	3534	3578	3530	3578	3536
		3556		3553		
Chlorfenethol	3575	3428	-	-	3610	3450
	(3580)*	(3425)*				
Benzhydrol	-	3335	-	3396	3620	3480
		3400		3334		
4,4 -Dichloro benzhydrol	-	3288		-	3618	3472
		3350				
Triphenyl methanol	-	3472	-	-	3610	3480

*In thin film obtained by rapid cooling of molten solid.

absorption at 3605 cm^{-1}. It is worthwhile to note a less obvious, but very important,point. The dimeric OH frequencies in solutions are closer in value to those in solid phase (Table I). Possibly, the configurations of associated structures in the solid phase are such that the OH very nearly behave like dimers in solutions.

It is apparent from Table I that the position of free OH seems to be considerably sensitive to the molecular structure. The monomerie OH of chlorfenethol shifts to relatively lower frequency presumably because of electron withdrawal by the CH_3 group[24] at the α-position. Fox and Martin[25] and Barnard[26] et al reported free OH of phenol in CCl_4 as 3610 cm^{-1}. The triphenyl methanol gives free OH at 3610 cm^{-1}. It should be pointed out that the free OH frequency in either benzhydrol or $4,4^1$-dichloro derivative (ca 3620 cm^{-1}) is higher (+10 cm^{-1}) than that of phenol. The OH bond in the hydroxyl group is not totally coplanar, resulting weaker conjugation between the unshared electrons of the OH oxygen and the π electrons of the phenyl rings.

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