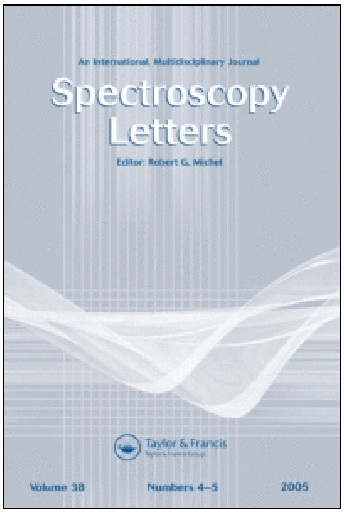

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SOLVENT EFFECT ON THE ISOTOPIC RATIOS ν^{o}_{OH}/ν_{OD} AND A_{OH}/A_{OD} IN A TETRACHLOROSUBSTITUTED MANNICH BASE

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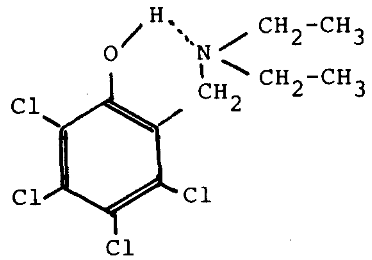
INTRODUCTION

Mannich bases are compounds formed from phenols and amines, characterized by intramolecular hydrogen bonds whose strength depends on the substituent implanted on the phenol ring; moreover, as shown by uv measurements, the strength of the interaction for a given phenol derivative depends strongly on the solvent[1-3]. In this work, we have studied the ir spectra of 2,3,4,5-tetrachloro-6-[(diethylamino)methyl]phenol ($TCMB_H$)



and the analogous O-deuterated compound ($TCMB_D$) in several organic solvents. The uv spectra show one main band lying at 304-305 nm with a shoulder of low intensity at

330 nm, indicating that almost all the hydrogen bonds are of the OH...N type; in acetonitrile, a second band at 330 nm was detected and in this solvent about 20% of proton transfer complexes are formed at 298 K [4]. The dipole moment of $TCMB_H$ dissolved in benzene (5.10 D) [5] suggests however that the OH...N bond is strong, in agreement with infrared studies performed on similar molecules[6,7].

EXPERIMENTAL

The ir spectra were recorded with a Perkin-Elmer 580B spectrophotometer. The concentrations of TCMB ranged from 0.1 to 0.4 M and the cell thickness from 0.01 to 0.04 cm. The synthesis and deuteration of the product, the purification of the solvents and the experimental procedure were described in a previous work[7].

RESULTS AND DISCUSSION

In all the solvents, the ν_{OH} band is broad and characterized by two main components, observed around 2500 and 1900 cm^{-1} and depending upon the nature of the solvent (figure 1). The intensity ratio of these two absorptions depends on their separation and this strongly suggests that they originate from a Fermi resonance. In the deuterated derivative, one main absorption was observed (figure 2).

Table 1 lists the wavenumbers of the two bands (ν^S_{OH} and ν_F), their separation (Δ) and intensity ratio (R) along with the ν_{OD} values observed in the deuterated compound.

The energy separation between the perturbed levels can be expressed by

$$\Delta = (\Delta_o^2 + 4W^2)^{1/2}$$

where Δ_o represents the separation between the harmonic

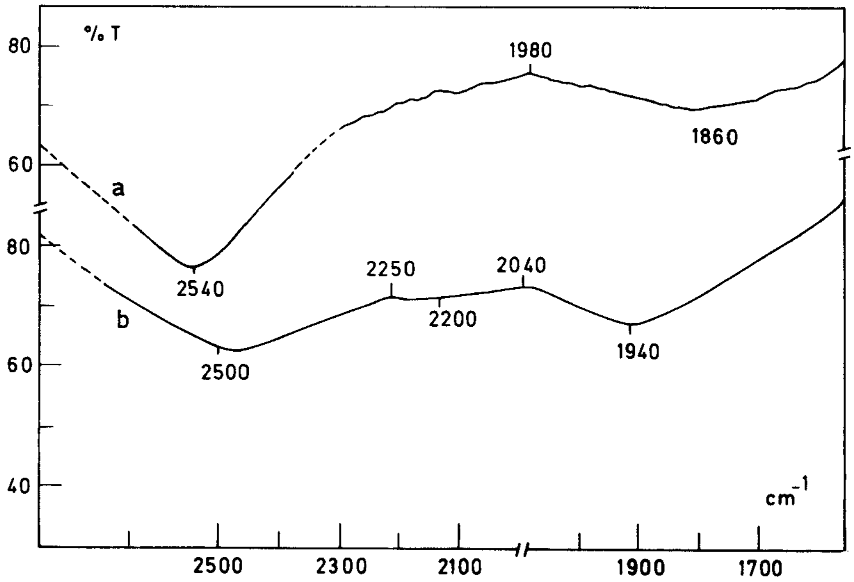


FIG. 1 IR spectrum (2800 cm^{-1}) of $TCMB_H$ dissolved
a) in cyclohexane (C = 0.1 M, d = 0.6 mm)
b) in $C_2H_4Cl_2$ (C = 0.5 M, d = 0.3 mm)
------ indicates an absorption of the solvent.

levels and W the Fermi coupling coefficient[8]. The W values can be computed from the expression of Bertran et al.[9] based on the assumption that the intensity of the forbidden transition is zero :

$$R = \frac{\Delta + (\Delta^2 - 4W^2)^{1/2}}{\Delta - (\Delta^2 - 4W^2)^{1/2}}$$

The real frequencies of the two components of the Fermi doublet are calculated from the equation

$$\nu^o_{OH} = \frac{\nu^s_{OH} + \nu_F}{2} \pm \frac{\nu^s_{OH} - \nu_F}{2} \; \frac{R-1}{R+1}$$

The computed values of W, Δ_o, ν^o_{OH} and ν^o_F are indicated

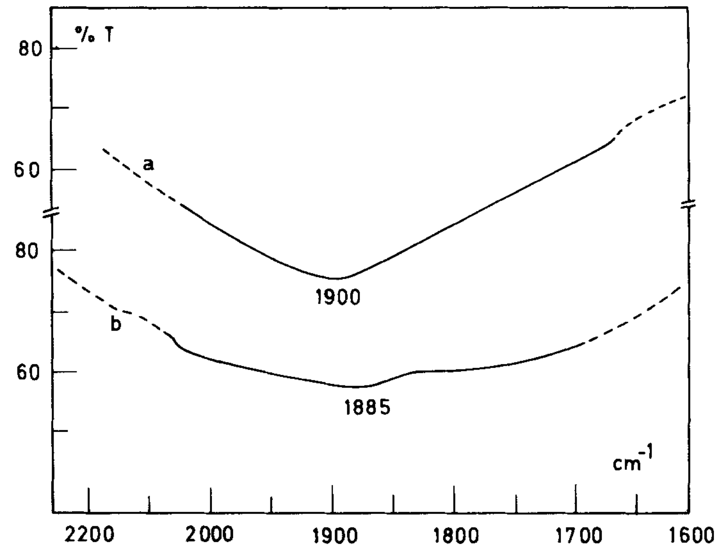


FIG. 2 IR spectrum (2200-1600 cm^{-1}) of TCMB$_D$ dissolved
a) in CS$_2$ (C = 0.17 M, d = 0.3 mm)
b) in C$_2$H$_4$Cl$_2$ (C = 0.22 M, d = 0.4 mm)

TABLE 1 Experimental ν^S_{OH}, ν_F, Δ, R and ν_{OD} values

Solvent	ν^S_{OH} (cm^{-1})	ν_F (cm^{-1})	Δ	R	ν_{OD} (cm^{-1})
n-hexane	2560	1850	710	10.5	1945
cyclohexane	2540	1860	680	10.0	1935
CCl$_4$	2510	1870	640	8.6	1915
C$_2$Cl$_4$	2510	1880	630	8.3	1915
CS$_2$	2500	1880	620	7.8	1900
C$_2$HCl$_3$	2500	1920	580	5.9	1900
CHCl$_3$	2490	1940	550	4.5	1885
CH$_2$Br$_2$	2500	1940	560	4.2	1885
C$_2$H$_4$Cl$_2$	2500	1940	560	3.4	1885
CH$_3$CN	2470	1940	530	2.9	1880

TABLE 2 W, Δ_o, ν^o_{OH}, ν^o_F, ν^o_{OH}/ν_{OD} and A_{OH}/A_{OD} values

Solvent	W (cm^{-1})	Δ_o (cm^{-1})	ν^o_{OH} (cm^{-1})	ν^o_F (cm^{-1})	ν^o_{OH}/ν_{OD}	A_{OH}/A_{OD} *
n-hexane	200	586	2491	1912	1.281	1.93
cyclohexane	196	556	2478	1922	1.280	1.86
CCl_4	196	507	2443	1936	1.276	1.80
C_2Cl_4	196	494	2442	1948	1.275	1.84
CS_2	197	478	2424	1951	1.276	1.68
C_2HCl_3	204	412	2416	2004	1.271	1.70
$CHCl_3$	213	349	2392	2040	1.269	1.51
CH_2Br_2	220	345	2395	2047	1.265	1.50
$C_2H_4Cl_2$	234	305	2373	2067	1.258	1.47
CH_3CN	231	258	2334	2076	1.238	1.40**

* Approximate values owing to the broadness of the band, the absorption of the solvents and the presence of OH derivative in the deuterated base.

** The total integrated intensity of the broad absorption contains also some contribution of the ν_{NH^+} (or ν_{ND^+}) vibration which is observed at 2800-2700 (2100-2000) cm^{-1} [10].

in table 2; this table also lists the isotopic ratio of the frequencies (ν^o_{OH}/ν_{OD}) and of the intensities (A_{OH}/A_{OD}).

The ν^o_{OH} values are 15 to 30 cm^{-1} lower than for the analogous 2,4,5-trichloro derivative[7] and this shows that in TCMB$_H$, the strength of the intramolecular OH...N bond is somewhat higher. This is in agreement with the increment of dipole moment brought about by hydrogen bond formation, which is 1.82 D for TCMB$_H$ and 1.67 D for the trichloro derivative[5].

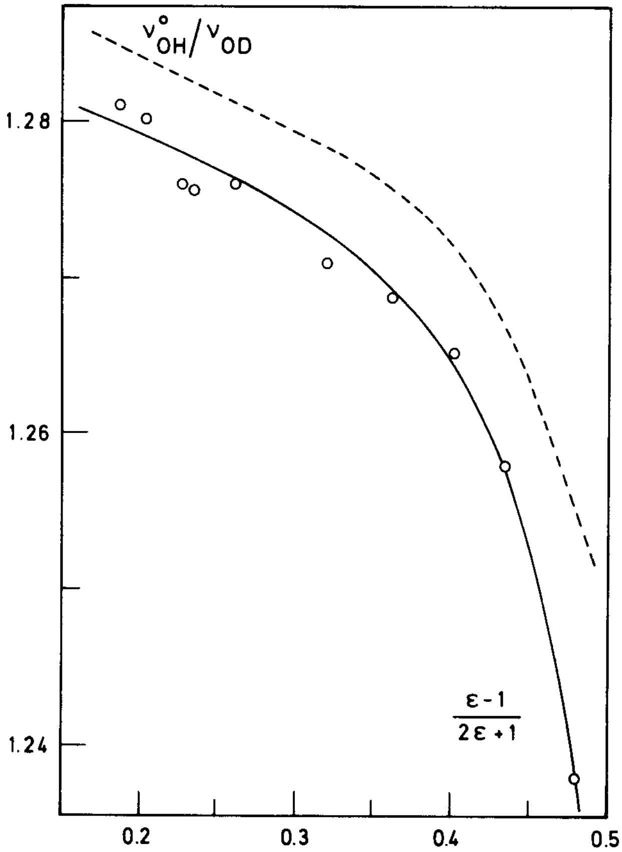


FIG. 3 ν^{o}_{OH}/ν_{OD} versus $(\varepsilon-1)/(2\varepsilon+1)$
——— TCMB
----- 2,4,5-trichloro Mannich base

The results of table 2 indicate that the strength of the intramolecular OH...N bond increases with the polarity of the medium, some proton transfer species being formed in acetonitrile. This increase is also consistent with a decrease of the isotopic ratio of the frequencies and this behaviour clearly appears from figure 3 where the ratio ν^{o}_{OH}/ν_{OD} has been plotted against

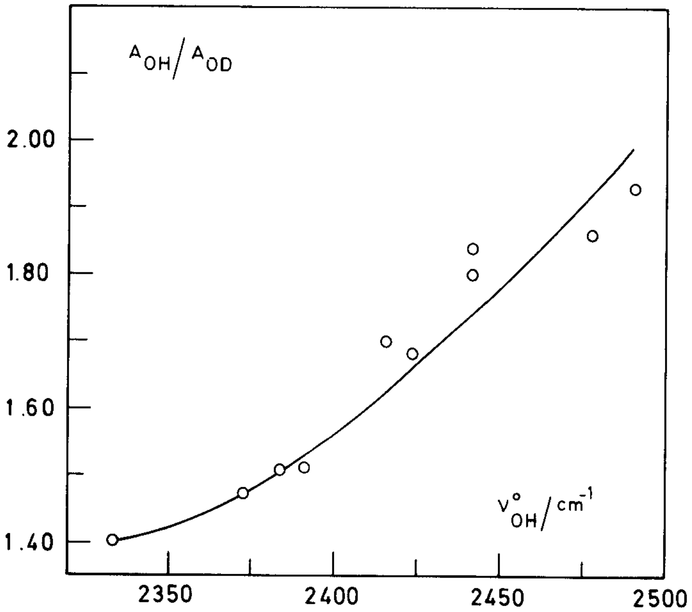


FIG. 4 A_{OH}/A_{OD} versus the computed values of ν_{OH}

the Onsager parameter $(\varepsilon-1)/(2\varepsilon+1)$ of the solvent. As shown indeed by Novak[11], there is a systematic decrease of the isotopic ratio when the hydrogen bond becomes stronger. In this figure, the variation of the same ratio is shown for the 2,4,5-trichloro-Mannich base and the somewhat higher ν^{o}_{OH}/ν_{OD} values obtained for this molecule are also consistent with a weaker OH...N bond.

The results presented in table 2 also show that the isotopic ratio of the intensities is lower than the harmonic ratio. Although the experimental values are less accurate than the isotopic ratio of the frequencies, figure 4 indicates that the A_{OH}/A_{OD} values show a net tendency to decrease when the hydrogen bond becomes stronger.

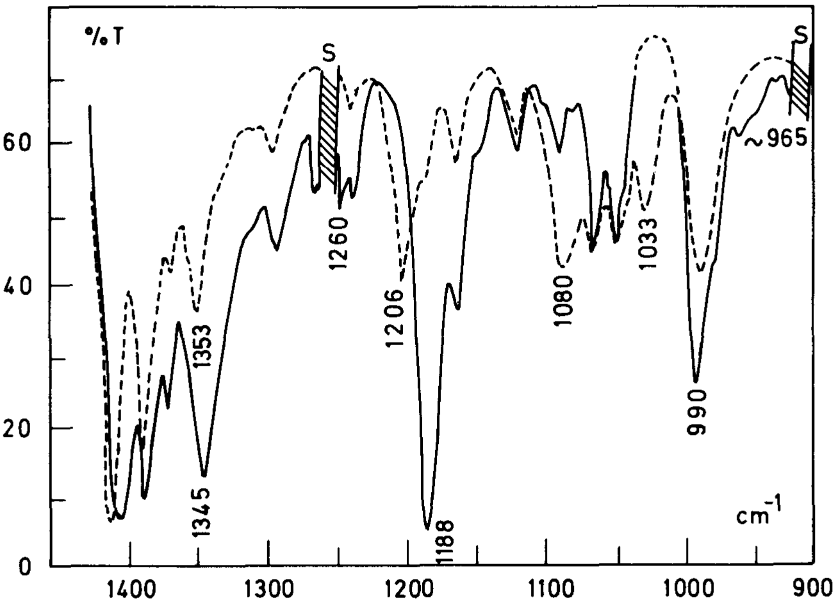


FIG. 5 IR spectrum (1450-900 cm^{-1}) of
—— $TCMB_H$ (C = 0.1 M, d = 0.6 mm)
--- $TCMB_D$ (C = 0.1 M, d = 0.4 mm)
Shaded area indicates absorption of the solvent.

As discussed in earlier works[12,14], the broad absorption observed between 3000 and 1600 cm^{-1} is typical for medium-strong hydrogen bonds and originates from a Fermi resonance between the ν_{OH} fundamental and overtones or summation frequencies of the δ_{OH} or γ_{OH} vibrations. The ir spectra (1450-900 cm^{-1}) of $TCMB_H$ and its deuterated analogue dissolved in cyclohexane are reproduced in figure 5.

The δ_{OH} vibration is observed at 1188 cm^{-1} and is shifted to 1033 cm^{-1} in the OD derivative. This vibration is rather insensitive to the strength of the hydrogen bond and appears to be also mixed with the

ν_{19} (1400 cm^{-1}) and ν_{14} (1345 cm^{-1}) ring modes and with the ν_{C-O} (1260 cm^{-1}) mode.

The band at 965 cm^{-1} which disappears on deuteration is assigned to the γ_{OH} vibration. The value of this frequency is approximately half the ν_F^o value in the same solvent (= 961 cm^{-1}) and from this, it can be concluded that Fermi resonance probably arises from an interaction between the ν_{OH} and $2\gamma_{OH}$ levels. In this case, the frequency of the computed maximum coincides better with the frequency of $2\gamma_{OH}$ than that of the minimum lying at 1980 cm^{-1} (figure 1). In more polar solvent, secondary bands are observed between 2300 and 2200 cm^{-1} which possibly arise from a $\nu_{OH} \leftrightarrow 2\delta_{OH}$ interaction.

Unfortunately, owing to the absorption of the solvents and the overlapping with the trigonal ring breathing mode, the γ_{OH} vibration could not be observed in all the solvents used in this work.

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