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Note

IR spectra and hydrogen bonding in tetritols

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Abstract

The out-of-plane (τ) H-vibration bands in spectra of polycrystalline films of two isomeric alditols, *meso*-erythritol and D,L-threitol, were recorded at 300 K and at 20 K for both OH and OD compounds and the H-band parameters were used for the evaluation of the relative strengths of the H-bonds in the crystals of two tetritols. Unlike erythritol, in the crystals of which all the H-bonds are strong, threitol contains additional weak H-bonds. This fact might be related to the strong water absorption capability of D,L-threitol, as compared to the reluctance of *meso*-erythritol to absorb water. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: IR spectroscopy; Hydrogen bonding; Tetritols; Water absorption

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1. Introduction

As a part of a research effort to relate the infrared spectra of mono- and polyhydric alcohols to their structure in the solid state and in solution, and an attempt to infer from these the hydrogen bonding characteristics of these substances, we now report a study of two isomeric tetritols, *meso*-erythritol and (racemic) D,L-threitol. Both have different crystal structures [1–5] and melting points (120 °C for erythritol and 90 °C for threitol [6]), and differ significantly in their water absorption ability from a wet atmosphere. Threitol sorbs water avidly whereas erythritol hardly does so at all, although both are quite water-soluble [6]. This behaviour is expected to be due to differences in structural and bonding aspects of the crystals, investigated in this study.

2. Experimental

The crystals of pure tetritols were commercial samples (Aldrich); the OD-form (90–95%) was obtained by deuterium exchange with deuterium oxide [7] or by recrystallization from Et OD (Aldrich). The polycrystalline films were prepared from the melt between potassium bromide plates at 80–120 °C. Consecutive recrystallization had no effect on the recorded spectra. Low temperatures measurements were attained with a Displex CS-202 (Air Products) closed cycle helium refrigerator and the accuracy of the temperature measurements was ±3 K. IR spectra were recorded on a Bruker 113v FTIR spectrometer at a resolution of 1 cm^{-1}, using a DTGS detector.

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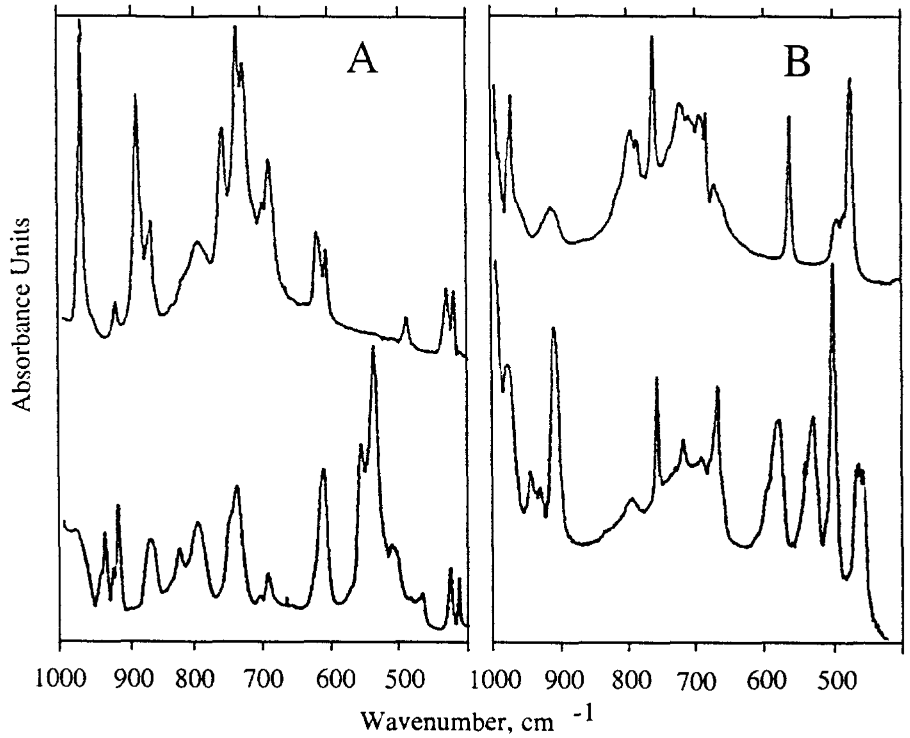

Fig. 1. IR spectra of crystal films at 20 K of *meso*-erythritol (A) and D,L-threitol (B): upper spectra, OH crystals and lower spectra, OD crystals.

Spectra of the crystals varied gradually and reversibly with temperature with good reproducibility.

3. Results

The infrared spectra at 20 K, of erythritol and of threitol, in the wavenumber range below 950 cm^{-1}, are shown in Fig. 1A and B respectively and their band frequencies and widths are summarized in Table 1. There are two structured bands of medium intensity in the erythritol spectrum near 870 and 720 cm^{-1}. The threitol spectrum shows four bands, three of which are weak, single and rather narrow and one (near 700 cm^{-1}) broad and well-structured. The strong bands close to 1000 cm^{-1} in both spectra are related to in-plane OH-bending vibrations and are not discussed here. The most important fact is that, in the low frequency range, the spectrum of threitol shows two more bands as compared to the erythritol spectrum. All the bands under consideration disappear on deuterium exchange (see Fig. 1), confirming their assignment to the OH vibrations. As is usual for out of plane τ -vibrations, they all shift to higher frequencies at lower temperatures (the wider threitol band

Table 1
Parameters of τ-bands of *meso*-erythritol and D,L-threitol and calculated H-bond energies

	D,L-threitol							*meso*-erythritol	
T (K)	τ	γ	τ^{a}	τ	γ	τ	γ	τ^{b}	τ^{a}
300	870	35	687	561	7.8	473	10.1	884, 864	705
20	915	24	726	564	6.3	475	8.2	888, 867	738
$-\Delta H$	48		31	18		12		48[c]	32

T = temperature; τ = peak frequency; γ = band width (cm^{-1}).
[a] A broad (100 cm^{-1}) band with complex temperature at the low temperature.
[b] A doublet.
[c] Calculated with the mean frequency of the doublet.
ΔH is the H-bond energy in $kJ \cdot mol^{-1}$ (see text).

near 870 cm^{-1} shifts more than the narrow 560 cm^{-1} and 473 cm^{-1} bands) [8,9]. Therefore their assignment to these modes is beyond doubt.

It should be noted that after crystallization from the melt of the commercial sample of D,L-threitol the band near 660 cm^{-1}, in nujol, disappears and a new narrow band of medium intensity appears at 765 cm^{-1} in the spectrum of the polycrystalline film. The frequency of the latter is independent of the temperature. This observation may be related with a possible change of the composition: the racemic D,L-threitol yields a mixture of D- and L- crystals [5] when crystallized from the alcohol. These changes may occur also upon crystallization from the melt.

The bands which are discussed below are not affected by the experimental procedure when compared with the spectrum of the initial sample in nujol.

4. Discussion

The frequencies of the out-of-plane proton vibration τ(OH) are known to be related to the H-bond energy (the enthalpy of H-bond formation in liquids) by the relation:

$$-\Delta H = 0.67 \times 10^{-4} \Delta\tau^2 \qquad (1)$$

where the frequency change is $\Delta\tau^2 \equiv \tau_H^2 - \tau_O^2$, the subscripts H and O pertaining to H-bonded and free molecules respectively, with $-\Delta H$ in kJ · mol^{-1} and τ in cm^{-1} [9]. This relationship is also valid for the evaluation of the H-bond energy in crystals [10], provided they are close to linear. The accuracy of this estimation is ± 4 kJ · mol^{-1} at best, largely because the frequency of τ_O for the free OH group in these systems is not established. For all four OH-groups, the same $\tau_O = 200$ cm^{-1} was assumed as for common gas phase monohydric alcohols [11]. The absolute values of $-\Delta H$ may be overestimated because, taking the reference τ_O-value for the gas phase, disregards restrictions on the torsional amplitude in condensed phases. The H-bond energies calculated by Eq. (1) are also given in Table 1.

The variety of H-bonds in the crystals of these two compounds have O · · · O distances in the range of 267–276 pm [2,5] and according to [12] the τ frequencies should fall in the range of 950–750 cm^{-1} and the range of H-bond energies is expected to be from 35 kJ · mol^{-1} to 55 kJ · mol^{-1}. Indeed, the spectroscopic considerations indicate that the energies of the strongest H-bonds in threitol crystal are in the range of 50 kJ · mol^{-1}, of the same strength as in the crystal of *meso*-erythritol (Table 1). However, the two low frequency OH modes in threitol crystals indicate the existence of two additional, relatively weak H-bonds with energies of 12–18 kJ · mol^{-1}.

The intensity of τ-bands does not depend on the frequency [8,9]. Judging by the relative intensity of the bands near 700 cm^{-1}, the strength of the majority of H-bonds in both tetritol crystals is about 30 kJ · mol^{-1}. Hydrogen bonds of such strength are unusual for unsubstituted alcohols, where $-\Delta H \approx$ 23 kJ · mol^{-1}. This strengthening can be attributed to a cooperative effect since, in the spectra of both tetritols, these bands as well as the one near 870 cm^{-1} in erythritol, reveal structures that can be assigned to the neighbour interactions in H-bonded chains. This is in good agreement with structural data since infinite H-bonded chains were found in both threitol and erythritol crystals (all H-bonds are two-centered and intermolecular) [2,3,5]. However, the simultaneous existence of very strong and very weak H-bonds in threitol crystals is at first established by the spectroscopic measurements and is not indicated by the structural studies. The fact that the low frequency bands are single and narrow leads us to conclude that these H-bonds are isolated and not affected by neighbour interactions. Moreover, their small bandwidth (≤ 10 cm^{-1}) may indicate that the corresponding H-bonds are included in a rather rigid structure.

For threitol, the ratio of intensities of single H-bands near 870, 561 and 473 cm^{-1} is 1:1:2 ($\pm 10\%$), giving an estimate of the abundance ratio of strongest to weakest H-bonds [1]. Two explanations for the formation of weak H-bonds in threitol crystals may be forwarded. The first involves the loss of proton acceptance capability of the oxygen atom of a hydroxyl group which is already involved in a very strong H-bond. For example, perfluoro-*tert*-butanol, which is the strongest H-bond donating acid among the fluoroalcohols, is not selfassociated at all [13]. The second one is a possible deviation of the H-bonds from linearity. According to [3,5], some of the H-bonds of threitol are non-linear ($\angle$O–H · · · O $\approx$ 145–155°), while in erythritol crystals there are no H-bonds with angles less than 164° [2].

The existence of the weak ('non saturated') bonds in threitol and not in erythritol would also explain the enhanced water sorption capacity of the former [6]. The water molecule is a strong enough base (in terms

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[1] For erythritol the latter were not observed.

of H-bond formation) and can easily break these weak H-bonds and be absorbed by crystal. It should be noted that the IR spectra of the two tetritols in solution in the strong bases dimethyl sulfoxide and pyridine, do not exhibit differences attributable to differences in the strengths of the hydrogen bonds formed [14].

We also note a peculiarity in the threitol spectrum: the structure of the bands is very significantly altered upon D-exchange. This may indicate a rather unusual structural change in the crystal which is worthy of further attention.

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