

Near-Infrared Spectroscopic Study of Hydrogen Bonding in Chiral and Racemic Octan-2-ol

Miroslaw A. Czarnecki*

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

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The effect of temperature on self-association of (*R*)-(-)-octan-2-ol, (*S*)-(+)-octan-2-ol, and the racemic mixture in the pure liquid phase has been studied by two-dimensional (2D) Fourier transform near-infrared (FT-NIR) correlation spectroscopy. Both the conventional FT-NIR and 2D correlation spectra of pure enantiomers and the racemic mixture are identical to each other and do not reveal the chiral discrimination effect. The similarity of temperature relationships of population of the free OH groups for the optically active and racemic samples confirms the above conclusion. Of particular note is that the asynchronous spectra of all studied samples develop the peaks due to the free terminal OH groups in the open chain associates. This observation reveals a remarkable population of the linear species. The comparison of present results with previous studies on other isomers of octanol indicates that the degree of self-association decreases upon branching in the order octan-1-ol > octan-2-ol > octan-3-ol.

Introduction

There is a common agreement that the vibrational spectra of pure enantiomers are identical to each other.^{1–3} Also, the spectra of optically active and racemic alcohols in dilute solutions do not reveal any differences.^{1,2} On the other hand, the spectra of chiral and racemic alcohols at higher concentrations or in the pure liquid phase may show some differences due to the chiral discrimination. Herndon and Vincenti examined infrared (IR) spectra of optically active and racemic butan-2-ol in CCl₄.¹ At all concentrations (0.005–0.2 M), spectra of the pure enantiomers were identical with each other. In contrast, the authors observed significant decreases in intensities of hydrogen-bonded OH stretching bands in the racemic mixtures. As a result, the equilibrium constants for dimer and oligomer formation were noticeably lower in the case of racemic solutions.¹ Unfortunately, the authors did not explain the origin of the interactions responsible for the large observed anisometric effect. An opposite effect was observed by Walden et al. for a few optically active secondary alcohols with a chiral C atom in the α -position.² The authors suggested that the hydrogen bonding of racemic alcohols is favored by entropy; the construction of an associated chain from two different enantiomers allows more possible arrangements than the construction of isoconfigurational chains.² Recently, a chiral self-recognition effect in the gas phase was observed in supersonic jet Fourier transform (FT) IR spectra of glycidol.³ It has been reported that this effect leads to marked differences in the absorption pattern of the OH stretching bands of *RR* (*SS*) vs *RS* glycidol dimers. In contrast, IR and ¹H NMR spectroscopic studies of hydrogen bonding of pantolactone in CCl₄ solution did not show any selective association between enantiomers.⁴ Recent reexamination of butan-2-ol in CCl₄ solutions and in the pure liquid state by IR and near-IR (NIR) spectroscopy also did not reveal any noticeable differences between the optically active and the racemic samples.⁵ As can be seen, the literature devoted to this subject does not present a uniform picture. Therefore, the influence of chiral discrimination on vibrational spectra requires additional studies.

This paper reports the effect of temperature on self-association of chiral and racemic octan-2-ol. As suggested by Walden et al., the differences in statistic probability of formation of homo- and heterochiral associates should increase with increasing degree of association.² Therefore, the experimental measurements were performed in the pure liquid phase. The spectra were collected in the NIR region since the bands due to different hydrogen-bonded forms are better separated at the level of overtones.⁶ Besides, the less associated species have the stronger overtones,^{6,7} and it is easier to monitor the changes in population of the free OH groups. The vibrational bands in the liquid phase are inhomogeneously broadened and often heavily overlapped with each other. To resolve all spectral features, the spectra were analyzed using the generalized two-dimensional (2D) correlation method.^{8,9}

Experimental Section

Spectroscopic Measurements. (*R*)-(-)-Octan-2-ol, (*S*)-(+)-octan-2-ol, and CCl₄ were purchased from Aldrich Chemical Co. (Germany). The chemicals were obtained at the highest purity (>99%) and were used as received. The FT-NIR spectra were recorded at a resolution of 4 cm⁻¹ on a Nicolet Magna 860 spectrometer equipped with a DTGS detector, and 512 scans were accumulated. The spectra of all samples were measured in a thermostated quartz cell (Hellma) of 5 mm thickness from 20 to 85 °C with a step of 5 °C.

Data Treatment and 2D Correlation Analysis. Prior to 2D correlation analysis, the spectra were corrected for the density change with temperature and intensity of the second overtone of the CH stretching band (~8300 cm⁻¹) was used as reference.¹⁰ The baseline fluctuations were minimized by a simple offset at 9000 cm⁻¹. The dynamic spectrum $A^d(\nu, T)$ was created by subtraction of a reference spectrum from an ordered series of the experimental spectra ($m = 14$). The spectrum recorded at the lowest temperature $\{A(\nu, 20\text{ °C})\}$ was used as the reference. The synchronous intensity $\Phi(\nu_1, \nu_2)$ was calculated as a cross-product of the dynamic intensity at two different wavenumbers (ν_1, ν_2), whereas the asynchronous intensity $\Psi(\nu_1, \nu_2)$ was computed as a cross-product of the dynamic

* To whom correspondence should be addressed. Fax: 48-71-3282348. E-mail: mcza@wchuwr.chem.uni.wroc.pl.

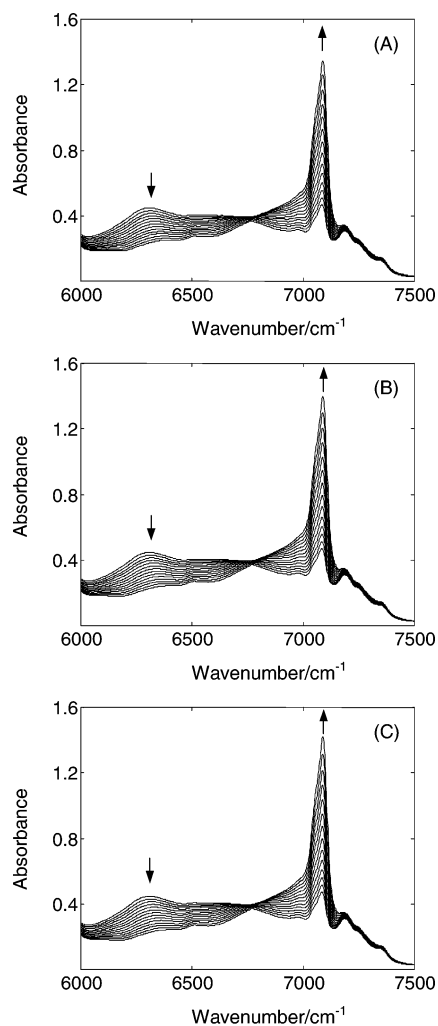


Figure 1. FT-NIR spectra of (*R*)-(-)-octan-2-ol (A), (*S*)-(+)-octan-2-ol (B), and the racemic mixture (C) from 20 to 85 °C (↑, intensity increases; ↓, intensity decreases).

intensity at ν_1 and Hilbert transform (H) of the dynamic intensity at ν_2 .¹¹

$$\Phi(\nu_1, \nu_2) = \frac{1}{m-1} \sum_{T_{\min}}^{T_{\max}} A^d(\nu_1, T) \cdot A^d(\nu_2, T) \quad (1)$$

$$\Psi(\nu_1, \nu_2) = \frac{1}{m-1} \sum_{T_{\min}}^{T_{\max}} A^d(\nu_1, T) \cdot [H \cdot A^d(\nu_2, T)] \quad (2)$$

The asynchronous spectra were multiplied by a sign of the corresponding synchronous spectra. Thus, in a synchronous spectrum, a positive peak at (ν_1, ν_2) indicates that the intensity changes at these two wavenumbers are in the same direction. A positive asynchronous cross-peak at (ν_1, ν_2) means that the spectral change at ν_1 occurs faster (earlier) than that at ν_2 . Negative synchronous and asynchronous peaks indicate the opposite. The 2D correlation analysis was performed using MATLAB 6.1 software (The Math Works, Inc.).

Results and Discussion

2D Correlation Analysis of Temperature-Dependent FT-NIR Spectra of Chiral and Racemic Octan-2-ol in the Pure Liquid Phase. Figure 1 shows FT-NIR spectra of (*R*)-(-)-octan-2-ol, (*S*)-(+)-octan-2-ol, and the racemic mixture from 20 to

TABLE 1: Frequencies (cm^{-1}) and Assignments of the NIR Bands Due to the OH Stretching Modes of Various Species of Octan-2-ol

species	FT-NIR spectra	2D correlation spectra	
		syn	asyn
monomer	7088	7089	7092
<i>trans</i> rotamer			7106
<i>gauche</i> rotamer			7081
free terminal OH			7046
dimer			6850
$\nu_{\text{CH}} + \nu_{\text{OH}}(\text{free})$	6511		
polymer	6309	6273	6230

85 °C. The spectra were recorded from 4500 to 11 000 cm^{-1} ; however, the analysis focused on the 6000–7500 cm^{-1} range. The positions and assignments of main bands in this spectral region are collected in Table 1. Raw FT-NIR spectra of all samples are very similar and do not reveal any discernible differences. Obviously, exploration of such fine effects requires more advanced methods of analysis. The 2D correlation approach is particularly suitable for resolving overlapped spectral features.^{8,9} The asynchronous spectrum is very sensitive to small differences in intensity changes at different wavenumbers. If two (or more) bands follow different patterns of intensity changes, they appear as separate features in the asynchronous spectrum, regardless of the separation in the conventional (one-dimensional) spectrum. Both the homochiral and the heterochiral associates with different properties that originate from the anisometric intermolecular interaction may exist in the racemic mixture.¹ In Figure 2A,B are shown the open dimers built of two identical (*SS*) and two different (*RS*) enantiomers, respectively. The structures were optimized at the RB3LYP/6-31G-(d) level. As can be seen, the strength of hydrogen bonding for both kinds of the dimers may differ due to distinct orientation of the hydrocarbon chains with respect to each other. Therefore, one can expect that the homo- and heterochiral associates break at different rates upon temperature elevation. This differentiation should give rise to new peaks in the asynchronous spectrum of the racemate. Furthermore, the population of the free OH groups in the chiral and racemic samples is expected to increase at different rates.

In Figures 3 and 4 are displayed the synchronous and asynchronous spectra, respectively, of (*R*)-(-)-octan-2-ol, (*S*)-(+)-octan-2-ol, and racemic octan-2-ol. Even a careful examination does not reveal any significant differences between these spectra. All spectra include identical numbers of correlation peaks. The positions of these peaks are the same within an experimental error for all studied samples (Table 1). In the synchronous spectrum, the autopeak dominates due to absorption of the free OH groups at 7089 cm^{-1} (“monomer” band). This peak is negatively correlated with the “polymer” band at 6237 cm^{-1} indicating that population of the free OH groups increases at the expense of the polymeric species. However, the presence of the asynchronous peaks (Figure 4) reveals that this process proceeds through the intermediate species. The sign of these peaks suggests that the intensity changes for the monomer band occur faster than those of any other species. On this basis, one can conclude that when the temperature rises the terminal hydrogen bonds break easier as compared to the internal ones as discussed previously in detail.¹²

Interestingly, the asynchronous spectra of all samples develop three peaks in the region of the monomer band (Figure 5). Two of these peaks originate from rotational isomerism of the OH group, while the third peak is due to the free terminal OH groups in the linear associates.^{13,14} The latter peak was observed only

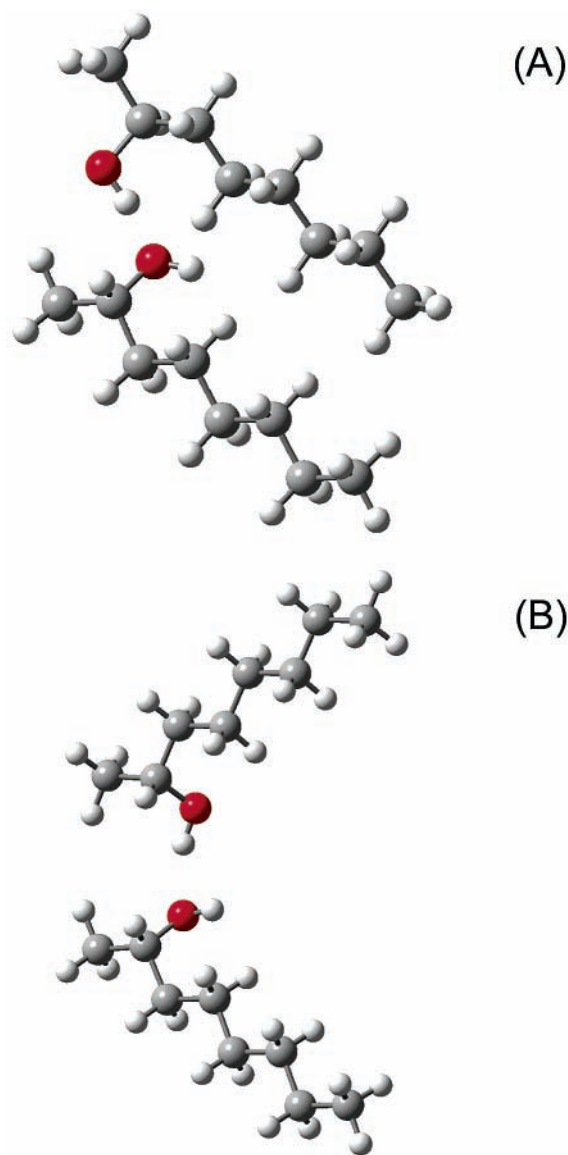


Figure 2. Hydrogen bonding between (A) two identical enantiomers (SS) and (B) between *R* and *S* enantiomers of octan-2-ol.

for branched alcohols like butan-2-ol¹³ and 2-methylpropan-2-ol¹⁴ and revealed the presence of a significant population of the open chain associates. In contrast, the correlation spectra of straight chain alcohols do not develop this peak due to a higher extent of self-association.^{14–16}

The heterospectral correlation analysis has the ability to enhance the spectral resolution beyond that obtained from the homospectral correlation analysis of individual samples.¹⁷ Because the FT-NIR spectra of pure enantiomers and racemic mixture were collected under the same experimental conditions, it was possible to perform the heterospectral correlation analysis between these data sets. The corresponding synchronous and asynchronous spectra (not shown) are similar to those obtained from homospectral 2D correlation analysis. Thus, 2D correlation analysis of temperature-induced spectral changes in optically active and racemic octan-2-ol does not provide any evidence for the chiral discrimination effect.

Temperature Dependence of the Degree of Dissociation of Chiral and Racemic Octan-2-ol. The molar absorptivity of the first overtone of the stretching band for the free OH group ($\epsilon_{2\nu(\text{OH})}$) has been determined from the spectra recorded at low concentrations of octan-2-ol in CCl_4 (0.002–0.01 M). The

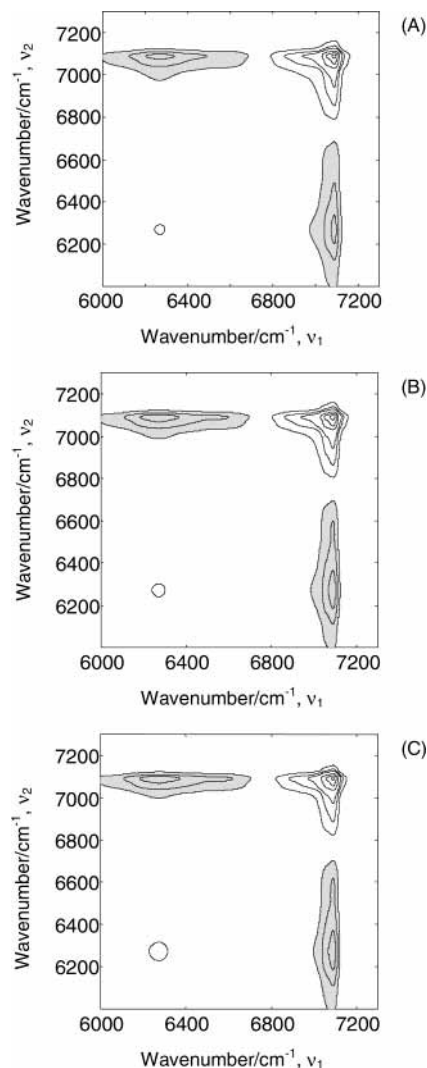


Figure 3. Synchronous 2D NIR correlation spectra of (*R*)-(-)-octan-2-ol (A), (*S*)-(+)-octan-2-ol (B), and the racemic mixture (C) from 20 to 85 °C. The negative peaks are shaded.

spectra of optically active and racemic alcohols at low concentrations are identical to each other;^{1,2,5} hence, the corresponding values of $\epsilon_{2\nu(\text{OH})}$ are the same. The determined values of $\epsilon_{2\nu(\text{OH})}$ were $102.3 \pm 1.0 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$ (integrated) and $1.80 \pm 0.05 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (at peak height) and were similar to those obtained for octan-1-ol¹⁶ and octan-3-ol.¹² The degree of dissociation, defined as a fraction of nonbonded OH groups, was evaluated using the same method as previously described.¹⁸ The integrated intensity of the monomer band was calculated by a direct integration. To separate the monomer band from the other spectral features, at first the spectra were Fourier self-deconvoluted. Figure 6 displays the temperature dependence of the degree of dissociation of (*R*)-(-)-octan-2-ol, (*S*)-(+)-octan-2-ol, and the racemic mixture. As can be seen, the differences between particular samples are smaller than 1% and do not exceed the experimental error ($\pm 2\%$). This result does not reveal differentiation in properties of optically active and racemic octan-2-ol and supports the conclusion obtained from 2D correlation analysis. The comparison of the degree of dissociation for octan-2-ol with corresponding data for others isomers of octanol^{12,16} evidences that the extent of self-association is reduced upon branching and decreases in the order octan-1-ol > octan-2-ol > octan-3-ol.

It has been suggested that the conformational flexibility of the monomer reduces the size of the chiral discrimination effect.³

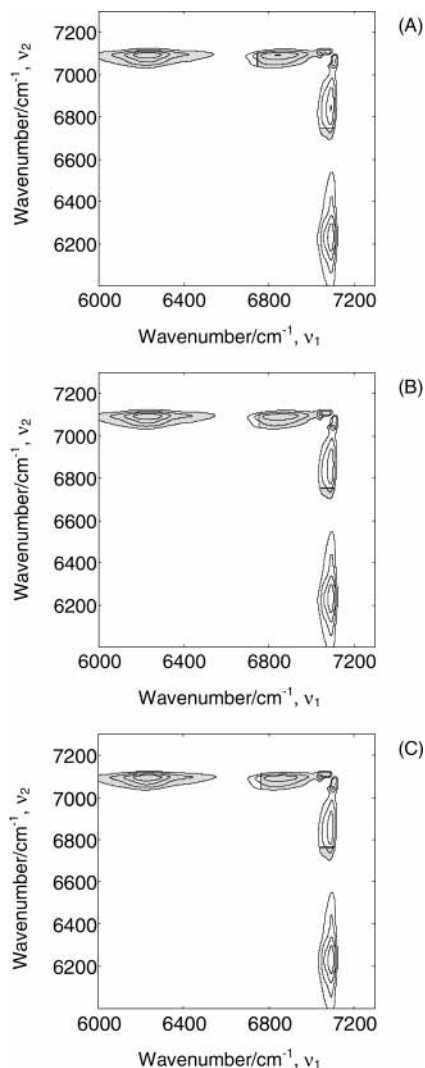


Figure 4. Asynchronous 2D NIR correlation spectra of (*R*)-(-)-octan-2-ol (A), (*S*)-(+)-octan-2-ol (B), and the racemic mixture (C) from 20 to 85 °C. The negative peaks are shaded.

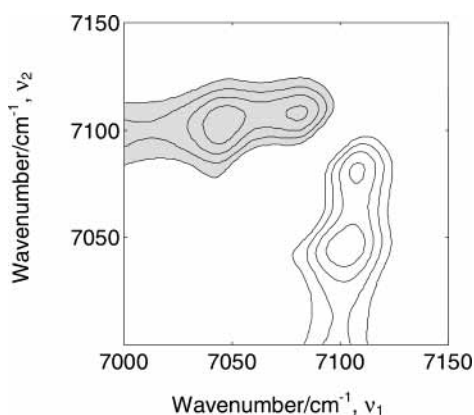


Figure 5. Localized view of the asynchronous 2D NIR correlation spectrum of racemic octan-2-ol from 20 to 85 °C. The negative peak is shaded.

The position and intensity of the second overtone of the CH stretching band (after normalization) did not change from 20 to 85 °C. Hence, it seems that the hydrocarbon chains do not undergo conformational changes in this temperature range. Probably more important is the conformational flexibility of the

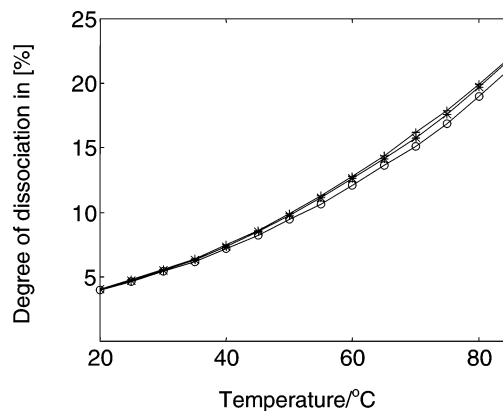


Figure 6. Temperature dependence of the degree of dissociation of (*R*)-(-)-octan-2-ol (O), (*S*)-(+)-octan-2-ol (*), and the racemic mixture (+).

OH group. Reduced flexibility of the OH group in glycidol enhances the chiral discrimination effect. On the other hand, the OH group in octan-2-ol has more freedom and as a result this effect is very small. The difference in the torsional potential of the OH group between the rotational conformers in alcohols was estimated to be 0.1–0.2 kJ/mol.¹⁹ This effect clearly appears in the asynchronous spectra of various alcohols giving rise to splitting of the first overtone of the monomer band ($\Delta\nu \approx 25 \text{ cm}^{-1}$).^{12–17} Hence, one can conclude that the magnitude of the chiral discrimination effect in octan-2-ol does not exceed 0.2 kJ/mol. This conclusion agrees with IR studies on racemic and (*R*)-2,2,4-trimethylpentan-3-ol, where enthalpies of association (ΔH) were found to be 5.5 and 5.7 kJ/mol, respectively.² The difference of 2.76 kJ/mol between homo- and heterodimers of butan-2-ol as reported by Herndon and Vincenti seems to be significantly overestimated.¹ It would correspond to $\Delta\nu \approx 230 \text{ cm}^{-1}$ ($1 \text{ J mol}^{-1} = 8.35 \times 10^{-2} \text{ cm}^{-1}$) and suggests that the hydrogen bonding in homo- and heterochiral associates is substantially distinct.

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