Tetrahedron. Vol 29, pp. 3019 to 3022 Pergamon Press 1973 Printed in Great Britain

HYDROGEN BONDING IN *CIS* AND *TRANS* 1-t BUTYLCYCLOHEXAN-4-OL

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(*Received UK* 26 *February* 1973; *Accepted for publication* 24 *May* 1973)

Abstract—The homogeneous autoassociation of *cis* and *trans* 1-t-butylcyclohexan-4-ol has been investigated by means of IR spectroscopy. The temperature and concentration dependences of this interaction have been examined in CCl_4 as solvent. The results demonstrate a lower degree of association in the case of the *cis* compound, especially because of the steric hindrance of the acceptor function of this substance. The enthalpy of associatio-n-ΔH is found at about 13 [kJ/mole] for the *trans* compound and may be somewhat lower for the *cis* alcohol. The absorbance of the associated OH band of the *trans* compound is constant with varying concentration and/or temperature, but for the *cis* alcohol it increases with increasing concentration and decreasing temperature.

INTRODUCTION

Starting from our interest in H-bonding, we investigated steric effects in a simple model of this interaction. The case described is the homogeneous association of cyclohexanols with axial or equatorial OH bonds, represented by *cis*-1-t-butylcyclohexan-4-ol and, on the other hand, by *trans*-1-t-butylcyclohexan-4-ol. It is a well-known fact,[1] that the t-Bu group strongly prefers an equatorial position on the cyclohexane ring. Thus the transformation from one chair conformation to the other is strongly hindered and the OH groups of the substances used here are either equatorially or axially arranged, but cannot change from one to the other position.

The interaction problem was investigated by IR spectroscopy, only CCl_4 being used as a solvent. The results describing the different behaviour of these substances are summarized and discussed.

RESULTS

The temperature and concentration dependency of the free OH str. bands were used to get information about the association behaviour. The frequencies of these bands vary in the temperature range between + 38° and − 18° for axial OH groups in about a linear relation from 3630 [cm^{-1}] to 3625 [cm^{-1}] and for equatorial ones in the same temperature range from 3625 [cm^{-1}] to 3620 [cm^{-1}]. If there is no association, the maximum optical densities of the OH str. bands of the two species are remarkably different. (Maximum molar decadic absorption coefficient of the *cis* substance = 88 [$l \cdot mole^{-1} \cdot cm^{-1}$], of the *trans* substance = 69 [$l \cdot mole^{-1} \cdot cm^{-1}$] at 20°).

These maximum absorption coefficients are remarkably temperature dependent. For the *cis* alcohol this coefficient amounts to 85; 88; 91; 93·5 [$l \cdot mole^{-1} \cdot cm^{-1}$] and for *trans* compound to 67; 69; 71; 72·5 [$l \cdot mole^{-1} \cdot cm^{-1}$] for the temperatures 38; 20; 0; − 18°, respectively. Contrary to this, the difference of the integrated absorption coefficients of the two alcohols is practically zero. Consequently, the band of the equatorial OH group has a greater halfwidth than that of the axial OH group and shows an unsymmetric shape, too.

In Fig 1 − ln α is drawn against the mole fraction x. The temperature T is used as a parameter. α is defined by the quotient ϵ_c: $\epsilon_\infty . \epsilon_c$ is the absorption coefficient at the concentration c, ϵ_∞ the same coefficient at an association free infinite dilution, practically lower than 0·02[mole/l]. The curves given in this figure are obtained from a least square treatment with a second-order approximation from the measured results; α is proportional to the rela-

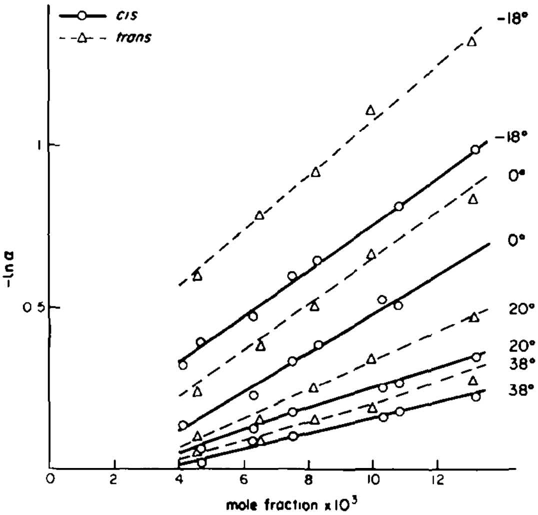

Fig 1. − ln α as a function of mole fraction x at different temperatures.

tive quantity of free OH groups or, respectively, for the number of H- bonds formed.

In Fig 2 the average number of molecules, forming one associating complex, is shown to depend on concentration. Again the temperature T is used as a parameter. These curves result from the Margule-Duhem formula,[2] $d \ln (1+x+f^{-1}x) = x d \ln \alpha$, which is solved by using the approximation for $-\ln \alpha$ from Fig 1. These results are confirmed for both of the compounds at 38° by osmometric measurements as described by Wachter and Simon.[3]

In Table 1 the values of the H- bond enthalpies ΔH are summarized. To determine these values, the formula

$$\frac{d \ln \epsilon_c}{dT} = \frac{\Delta H}{RT^2}$$

was used.

The shape of the free OH str. band of an 1:1 mixture of the *cis* and the *trans* substance, which is not separated in the overlapping single bands, does not show any change with varying temperature.

The associated OH str. band is shifted to lower wave numbers with decreasing temperature and increasing concentration. For the *cis* compound in the region of measurements given here, the shift $\Delta\nu_{OH}$ amounts from about 255 to 285 [cm^{-1}], and for the *trans* compound the respective values are about 240 to 300 [cm^{-1}]. The dimer band also appeared to be shifted more in the case of the *trans* compound (140 [cm^{-1}]) than of the *cis* compound (125 [cm^{-1}]).

Table 1. [kJ/mole] of homogeneous association

	trans				
mole Fraction · 10^{-3}	4·58	6·50	8·2	9·9	13·1
− 18°–0°	11·5	13·1	13·3	14·2	15·0
0°–20°	4·6	7·5	8·4	10·8	12·2
20°–38°	2·0	2·9	4·3	6·1	8·5
	cis				
mole Fraction · 10^{+3}	6·3	7·5	8·2	10·8	13·2
− 18°–0°	7·9	8·5	8·5	9·9	12·9
0°–20°	3·5	5·3	4·7		7·8
20°–38°	2·05	3·2	3·8	3·8	4·9

Both alcohols differ in the intensity of the associated OH band and its temperature dependence. In the case of the *trans* compound, in the investigated region of temperature and concentration, a constancy of the absorption coefficient is found by summarizing the area of this band, but in the case of the *cis* compound there is an increase of the intensity of the band in question with decreasing temperature as well as increasing concentration, without exceeding the value of the *trans* compound in the region investigated.

Additionally, the equilibrium constants of both of the systems, *cis*-cyclohexanol-γ-picoline and *trans*-cyclohexanol-γ-picoline, were measured. In the two systems equal constants were found at +39° as well as at −19°, namely 3·95 and 13·9 [l/mole] respectively, and consequently the same enthalpy ΔH = 14·0 [kJ/mole].

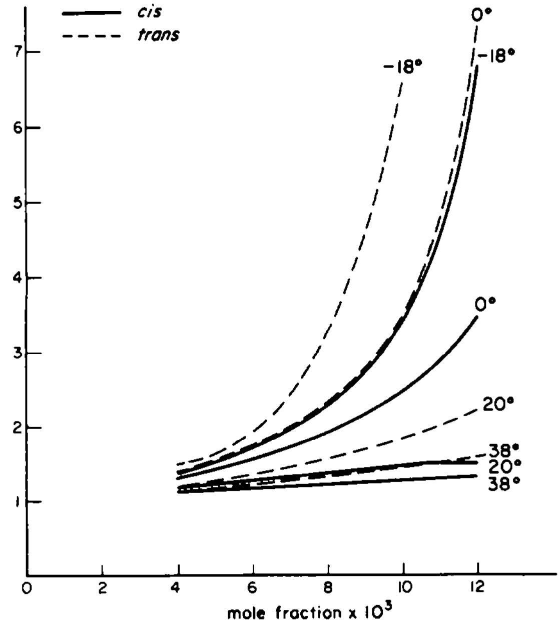

Fig 2. The average number f of molecules forming one associating complex as a function of mole fraction x at different temperatures.

DISCUSSION

The shape of the free OH bands is probably connected with the conformations, originating from rotation about the CO axis. The greater halfwidth of the OH band of the *trans* compound may be a consequence of this conformational heterogenety. The possible conformations are similar to those described for isopropanol.[4] The sharper band of the axial OH bond is generated, as discussed by Aaron and Raader,[5] by both of the two preferential conformations, in which the OH bonds are oriented away from the cyclohexane ring. The temperature dependence of the intensity of the free OH band cannot be explained by the higher vapour pressure of the alcohol, as done by Swenson,[6] because in our case the solvent possesses the higher vapour pressure. In our view, the increase of the density of the solution and the ensuing increase of concentration as well as the formation of stronger intermolecular interactions between the hydroxyl protons and the weak electronegative chlorine atoms, is the reason for this increase of intensity.

From Fig 1 it is clearly to be recognized that the *trans* substance is more capable of forming H-bonds.

The different behaviour of the two substances is probably based on the steric hindrance of the acceptor function only. The access to the free orbitals of the OH group in this case is hindered especially by the H atoms in the positions 3 and 5 of the ring; for, if we use our alcohols only as donators interacting with γ-picoline, both substances show the same equilibrium constant and the same value of ΔH. Therefore there cannot exist a steric hindrance for the donator function. Furthermore, because the shape of the overlapped free OH band of an 1 : 1 mixture of the *cis* and the *trans* alcohol does not vary with the temperature, neither of them is prefered to pass over into an associated state and for two different OH groups there exists the same number of well accessible and badly accessible acceptor groups. This result confirms the opinion of Aaron and Raader[5] about the arrangement of the axial OH bond only in one conformation, but does not confirm the opinion of Schleyer *et al.*[7] about the existence of a second conformation of the *cis* substance, in which the OH bond is directed towards the sixfold axis of the cyclohexane ring and the free orbitals of the oxygen should be oriented away from the ring. In this case, the donator behaviour also should be influenced by steric hindrance. The unequal absorbances of the associated bands are discussed in terms of steric arrangement. For the *trans* compound in every case of association nearly the same arrangement for all the OH—O bonds will exist. Probably only one of the conformations generated by rotation about the CO axis is preferentially enabled to take part in the H-bond. Furthermore it may be estimated from our results that only chain associations appear in this type of H-bond. This discussion is undoubtedly not sufficient to enlighten the rather unusual result of a constant absorption coefficient for an association band in the case of polymer association. We know no other example in which the same behaviour is described, but, all in all, only poor attention has so far been paid to the behaviour of association bands.

The curves in Fig 2 represent the average number of molecules forming an associated complex. Evidently this number is greater for the *trans* compound, which allows an uncomplicated structuring of any size of the associates. Accordingly we cannot describe the association behaviour of the *trans* compound by an selected set of only four equilibrium constants. In contrast, the degree of association of the *cis* compound is remarkably lower, not only because of the steric hindrance of the OH bond, but additionally because of the complication in arranging the cyclohexane ring and the bulky t-Bu group in the neighbourhood of the association centre. Therefore the lower values of the average number of *cis* molecules forming one associate are easy to understand. The values of ΔH, given in Table 1, increase with increasing concentration and decreasing temperature. The differences of ΔH between *cis* and *trans* compounds are in accordance with the differences of $\Delta\nu_{OH}$, and are to be interpreted in terms of a Badger-Bauer relation.[8]

There may be yet another aspect to this problem. Using the formula given above, the molecules changing from the monomer to the polymer state with decreasing temperature, are only allowed to enlarge already existing associated complexes, but not allowed to build up new ones. In the second case, $\ln \epsilon_c$ is not proportional to $\ln K$, and the calculated enthalpies are not correct. We know from Fig 2 that the magnitude of complexes in the case of *trans* compounds surpasses that of *cis* complexes. Therefore it will be easier for the *trans* compound to enlarge already existing complexes that it is for the *cis* compound, and the ΔH values of the substances seem to be different. The results obtained at the lowest temperatures and the highest concentrations may be nearest to reality.

Recently Mathur-DeVré[9] published NMR investigations of the monomerdimer equilibrium of our alcohols. It does not seem that the values reported there for-ΔH of dimerisation (31 and 26 [kJ/mole]) for *trans* and *cis* compound, respectively, are equal to those found here by means of IR spectroscopy for polymerisation. We believe our lower values to be in good accordance with those given by Mecke[10] for comparable alcohols (for instance-$\Delta H \approx 20$ [kJ/mole] for H-bonded polymerisation of benzylalcohol). In our work we also found the differences between the ΔH values of the alcohols to be somewhat smaller.

EXPERIMENTAL

The experimental work in the first parts of our investigation was done on the spectrometer UR 20, Zeiss Jena. All measurements were repeated and continued on the Beckman IR 12 with a wave number speed of 3·2 [cm^{-1}/min]. NaCl cells with 0·60 and 1·95 [mm] thickness were used. In order to vary the temp, a water thermostat jacket was used. Temps lower than + 15° were reached by a cooling apparatus described formerly.[11] The alcohols were obtained from the VEB Chemisches Kombinat Miltitz. Their purity was checked by gas chromatography. To control our weighing accuracy, we used the alcohol double band at 1324·5 and at 1368 [cm^{-1}] as an internal standard.

Acknowledgements—I am indebted to Prof. Dr. H. Pracejus for kindly given discussion on this subject, to Dr. G. Oehme for making the osmometric measurement and to W. Grimm for preparing the substances.

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