

INTRAMOLECULAR HYDROGEN BONDING
IN SOME VICINAL DERIVATIVES
OF TRICYCLO[4,4,0,0^{3,8}]DECANE (TWISTANE)* **

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The stereoisomeric 4-amino-5-hydroxytricyclo[4,4,0,0^{3,8}]decanes and their N,N-dimethyl derivatives have been prepared as models with various torsion angles. Intramolecular hydrogen bonding has been studied by IR spectroscopy in these compounds as well as in the stereoisomeric 4-hydroxy-5-methoxycarbonyl and 4-hydroxy-5-hydroxymethyl derivatives of the same system. Intramolecular hydrogen bonding was observed for the first time in a vicinal amino alcohol with a torsion angle 90° between the vicinal bonds. Some peculiarities of the hydrogen bonding, ascribed to the steric interactions in the twistane system, are discussed.

In one of our previous communications we have described the synthesis of some disubstituted derivatives of tricyclo[4,4,0,0^{3,8}]decane (twistane) and evaluated vicinal repulsive interactions between chosen substituents in this system². As we already pointed out, the twistane system allows one to investigate situations where the torsion angle between adjacent bonds is 30°, 90° and 150°. We have now made use of these fixed angles in the study of intramolecular hydrogen bonds (attractive interactions) between vicinal substituents.

It is well known³⁻⁸ that the shift of the hydroxyl band $\Delta\nu$, depends usually on the torsion angle, θ , between the vicinal donor and acceptor bonds. It is, however, still not yet clear whether there is reasonable correlation between θ and $\Delta\nu$ or not because suitable sufficiently rigid models with defined torsion angles are very scarce. It is also not known up to which θ the intramolecular hydrogen bond in a given system is capable of existing. Thus, *e.g.*, alcohols with vicinal hydrogen acceptors exhibit no hydrogen bonding when $\theta \sim 120^\circ$ whereas compounds with $\theta \sim 60^\circ$ have already $\Delta\nu$ of appreciable magnitude³. The situation was recently complicated by finding of Schleyer and collaborators⁹ that a conformationally fixed vicinal diol with θ close to 0° has an exceptionally low $\Delta\nu$ value. These authors compared the

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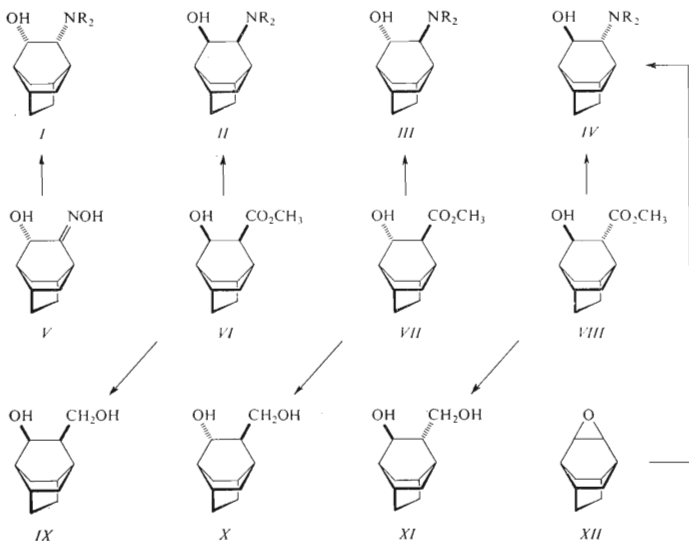
** Part of the results has been published in a preliminary form¹.

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observed $\Delta\nu$ values for vicinal diols in various rigid and semi-rigid systems with the Θ values computed using quantitative conformational analysis and found only a general trend of increasing $\Delta\nu$ with decreasing Θ , with a widespread scatter of points.

The torsion angles, however, were computed for 1,2-dimethyl substituted hydrocarbons instead for 1,2-diols, for which the $\Delta\nu$ values were observed. Since in principle there is generally a repulsion between the neighbouring methyls whereas there is an attraction between hydroxyls, the energetically most favourable geometry computed for the 1,2-dimethyl derivative may not be the same as for the diol. Also the fact that the values of Θ computed for the dimethyl derivatives, are almost the same as for the "parent" hydrocarbons may in some cases be misleading since some molecules might twist better in one direction (*e.g.* in the direction of repulsion of methyls) whereas the twist to the opposite direction (attraction of hydroxyls) may be more difficult.

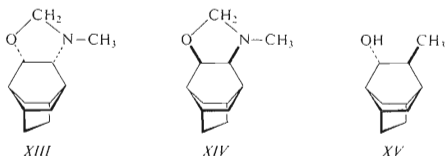
We prepared the four stereoisomeric amino alcohols *Ia*–*IVa* and dimethylamino alcohols *Ib*–*IVb* and studied their infrared spectra in the 3μ region, together with the hydroxymethyl derivatives *IX*–*XI* and the hydroxy esters *VI*–*VIII*.



SCHEME 1

a, R = H, *b*, R = CH₃

Synthesis of the compounds is depicted in Scheme 1. Three of the amino alcohols (*IIa-IVa*) were prepared by Curtius degradation of the corresponding hydroxy esters² (*VI-VIII*) whereas the remaining isomer *Ia* was obtained by catalytic reduction of the acyloin oxime *V*. The amino alcohol *IVa* was moreover obtained by ammonolysis of the epoxide *XII*. The configuration of the amino alcohols follows from method of their preparation and from their infrared spectra. The dimethylamino alcohols *Ib-IVb* were prepared by Clarke-Eschweiler methylation; in the case of the *exo,exo*-amino alcohol *IIa* the product contained about 75% of the corresponding oxazolidine derivative *XIV* and the *endo,endo*-isomer *Ia* afforded the oxazolidine



XIII even as the sole product. This oxazolidine formation in methylation of amino alcohol in which the vicinal functional groups are close to each other has been described¹⁰⁻¹² already several times. The methylation products of the *cis*-isomers were therefore directly reduced with lithium aluminium hydride to give the desired *N,N*-dimethylamino alcohols in good yields.

The infrared spectroscopic data are summarized in Table I, the corresponding $\Delta\nu$ values, together with the values obtained previously on systems representing other important torsion angles, are listed in Table II.

For obvious geometric reasons, the vicinal compounds with $\theta \sim 150^\circ$ exhibit no hydrogen bonding, as well as the already known^{5,12-14} compounds with $\theta \sim 120^\circ$.

The situation is, however, different with derivatives where $\theta \sim 90^\circ$. The spectrum of the amino alcohol *IIIa* exhibits, in addition to the free hydroxyl band at 3622 cm^{-1} , a band at 3604 cm^{-1} . The latter band lies on, or just outside of, the border of the region of the unassociated hydroxyl¹⁵ and the possibility of its belonging to a non-bonded rotamer cannot be *a priori* excluded. Therefore, we carried out a temperature dependence study. The intensity of the band at 3604 cm^{-1} decreases with increasing temperature whereas the intensity of the band at 3622 cm^{-1} increases. The enthalpy estimated from the plot of $\ln(B_1/B_2)$ against $1/T$ where B_1 and B_2 are apparent integrated intensities of the respective bands, is $\Delta H \sim 1.5 \text{ kcal/mol}$ in favour of the species, represented by the low-frequency band. If we take

“intrinsic” molar intensities B_1 and B_2 of the two bands as very similar (a reasonable assumption as the wave-numbers of the bands differ very little) we may roughly estimate that the species represented by the $3\,604\text{ cm}^{-1}$ band is disfavoured entropically by about 5. e.u. Clearly, this behaviour is completely consistent with the presence of a hydrogen bond in this species. Further support for the conclusion that the second band is due to the presence of hydrogen bond may be found in the spectrum of *endo*-4-hydroxy-*exo*-5-methyl(*r*-1)tricyclo[4,4,0,0^{3,8}]decane (*XV*) which is isosteric with the amino alcohol *IIIa*. This alcohol exhibits only one symmetrical band

TABLE I
Infrared Spectral Data

Torsion angle	Compound	$\nu(\text{OH})_{\text{free}} (\epsilon_f)$ cm^{-1}	$\nu(\text{OH})_{\text{bonded}} (\epsilon_b)$ cm^{-1}	$\Delta\nu(\text{OH})$ cm^{-1}
Amino alcohols				
30°	<i>Ia</i>	—	3 367 (49)	255 ^a
30°	<i>IIa</i>	—	3 375 (30)	248 ^b
90°	<i>IIIa</i>	3 622 (54)	3 604 (46)	18
150°	<i>IVa</i>	3 623 (64)	—	—
N,N-Dimethylamino alcohols				
30°	<i>Ib</i>	—	3 250 (12)	368
			3 440 (19)	178 ^c
30°	<i>IIb</i>	—	3 350 (47)	269 ^d
90°	<i>IIIb</i>	3 618 (58)	—	—
150°	<i>IVb</i>	3 619 (68)	—	—
Hydroxy esters				
30°	<i>VI</i>	3 615 (25)	3 520 (29)	95
90°	<i>VII</i>	3 624 (56)	3 608 (49)	16
150°	<i>VIII</i>	3 626 (97)	—	—
1,3-Diols				
30°	<i>IX</i>	3 629 (broad) (87)	3 585 (64)	44
90°	<i>X</i>	3 613 (59)	3 584 (66)	56, 29
		3 640 (86)		
150°	<i>XI</i>	3 622 (118)	—	—
		3 637 (76)		

^a Computed taking $\nu(\text{OH})_{\text{free}} 3\,622\text{ cm}^{-1}$ (in *IIIa*). ^b Computed taking $\nu(\text{OH})_{\text{free}} 3\,623\text{ cm}^{-1}$ (in *IVa*). ^c Taking $\nu(\text{OH})_{\text{free}} 3\,618\text{ cm}^{-1}$ (in *IIIb*). ^d Taking $\nu(\text{OH})_{\text{free}} 3\,619\text{ cm}^{-1}$ (in *IVb*).

TABLE II

Values of $\Delta\nu(\text{OH})$ (cm^{-1}) of Selected Model Systems with Given Torsion Angles θ between the C—OH and C—X Bonds

θ	System	X				
		NH ₂	N(CH ₃) ₂	OH	CO ₂ CH ₃	CH ₂ OH
0°		242 ^a	277 ^b	85 ^c	^d	^d
30°		248	269 ^e	78 ^f	95	44
60°		130 ^b	150 ^b	39 ^g	80 ^h	90 ^h
60°		95 ⁱ	150 ⁱ	32 ^j	25 ^h	90 ^h
90°		18	0	^d	15	29
120°		0 ^a	0 ^a	0 ^k	^d	^d

^a Ref.¹²; ^b ref.¹³; ^c ref.^{5,12}; ^d not known; ^e for *Iib*; ^f ref.¹⁷; ^g values for *cis*-1,2-cyclohexane-diol⁴; ^h ref.¹⁸; ⁱ ref.¹⁶; ^j ref.¹⁹; ^k ref.¹⁴.

at 3624 cm^{-1} . If the band at 3604 cm^{-1} in the spectrum of amino alcohol *IIIa* were due to the presence of free hydroxyl rotamers, there would be no reason for its non-existence in the compound *XV* in which the amino group is replaced by a methyl.

The relatively high value of ΔH is somewhat unexpected. It is comparable with ΔH found for the diequatorial *trans*-2-amino-*trans*-4-tert-butylcyclohexanol¹⁶ where the dihedral angle between the functional groups is $\theta \geq 60^\circ$ and $\Delta\nu \sim 100\text{ cm}^{-1}$. The explanation of this discrepancy may rest in the fact that ΔH values found in this way reflect not only the energy of the hydrogen bond as such but also the energetic

demands of the rotamers around the C—O and C—N bonds. Therefore the actual net enthalpy of the hydrogen bond is likely to be somewhat different from the enthalpy value found.

The spectrum of the corresponding *N,N*-dimethylamino alcohol *IIIb* exhibits only one symmetrical band of free hydroxyl at 3618 cm^{-1} . This is very surprising on first sight because the *N,N*-dimethylamino alcohols are known³ to form stronger hydrogen bonds than the parent amino alcohols. Nevertheless, this finding may easily be explained by a more detailed analysis of the steric situation in the hydrogen-bonded and non-bonded conformers: Whereas one of the non-bonded conformations is relatively free of steric strain, in the hydrogen-bonded form both methyl groups are pressed against the hydrogens at $C_{(2)}$ and $C_{(3)}$, thus causing a strain of prohibitive magnitude.

Let us now consider the *cis*-amino alcohols with $\theta \sim 30^\circ$. Here the $\Delta\nu$ value is already about 250 cm^{-1} for both the isomer *Ia* and *Iia*. This value is practically identical with the value of $\Delta\nu$ for *cis*-2-aminobicyclo[2,2,2]octan-3-ol¹² (Table II) for which an angle $\theta \sim 0-10^\circ$ is assumed^{20,21}. Clearly, in going from $\theta \sim 30^\circ$ to $\theta \sim 0-10^\circ$ one finds for amino alcohols no further increase in $\Delta\nu$. This fact is not likely to be due to inherent geometric differences between the systems used as models (slightly different valence angle deformation in twistane and bicyclo[2,2,2]octane systems) because this should result in an opposite effect. One possible explanation may be that the geometrically optimum planar chelate ring (with the shortest distance between the hydroxyl hydrogen and the acceptor atom) in a system with $\theta \sim 0^\circ$ is not the optimum conformation in terms of energy. In order to minimize eclipsing strain, the functional groups may tend either to increase the angle θ (Fig. 1a) and/or to rotate around the C—O and C—N bonds (Fig. 1b), thus increasing the distance between the hydrogen-bonded atoms and affecting very unfavourably the geometry of the chelate ring.

The spectra of *cis*-*N,N*-dimethylamino alcohols *Ib* and *Iib* represent a different picture. Whereas the latter isomer *Iib* has the bonded hydroxyl band at 3350 cm^{-1} , its epimer *Ib* exhibits a band at 3452 cm^{-1} and a weaker one at 3287

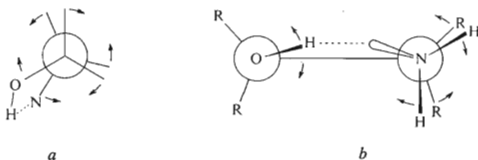
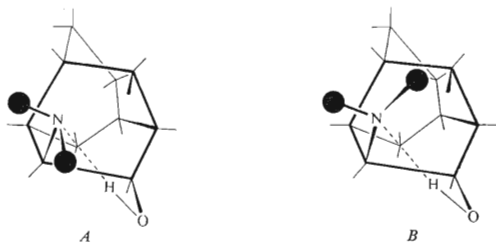


FIG. 1
 a By rotation around the C—C bond; b by rotation around the C—O and C—N bonds.

cm^{-1} which, as shown by dilution experiments, is not due to an intermolecular hydrogen bond. (Fig. 2).

Undoubtedly, two kinds of hydrogen-bonded species are present in the isomer *Ib*. Examination of models reveals that the N,N-dimethylamino group in this isomer is in a crowded position. One may visualize two non-eclipsed hydrogen-bonded conformers. In the conformer *A* the methyl groups are relatively unstrained whereas the geometry of the hydrogen bridge is not very favourable; on the other hand in the conformer *B* one of the methyl groups is in a sterically very bad situation, interacting with the $\text{C}_{(1)}$ and $\text{C}_{(2)}$ hydrogens. This interaction may bring the functional groups close to each other with resulting substantial increase in the $\Delta\nu$ value.



The hydroxy esters *VI–VIII* and hydroxymethyl derivatives *IX–XI* represent another class of compounds since the chelate ring in them is six-membered and its geometric requirements are somewhat different, allowing greater flexibility of the system. Both the ester *VII* and diol *X* with $\theta \sim 90^\circ$ exhibit a weak hydrogen bond (band at 3608 and 3584 cm^{-1} , respectively).^{*} Of the *cis* isomers ($\theta \sim 30^\circ$) only that with the *exo-4*-configuration (sterically unfavourable) of hydroxyl and the *exo*-

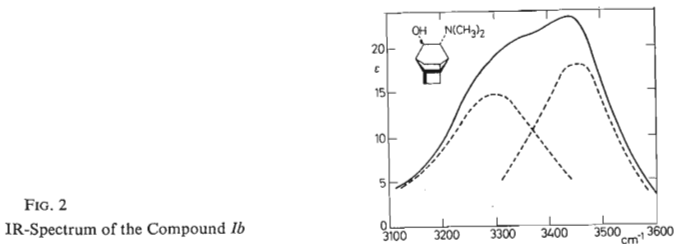


FIG. 2
IR-Spectrum of the Compound *Ib*

* A complicated β -hydroxy ester with $\theta \sim 90^\circ$ has been reported²² to have $\Delta\nu \sim 25 \text{ cm}^{-1}$.

-5-configuration of the methoxycarbonyl or hydroxymethyl group (sterically favourable) was available. Whereas the spectrum of the ester *VI* exhibits a "normal" $\Delta\nu$ value (95 cm^{-1}), the band of the bonded hydroxyl in diol *IX* is located at 3585 cm^{-1} ; this is the same wavelength as in the diol *X* which has $\Theta \sim 90^\circ$. This is puzzling since the lowest possible O—O distance in the isomer *IX* is about 2.1 Å whereas in *X* the two oxygens can approach each other only at a distance of about 3.7 Å. Two possible explanations of this unusual behaviour may be offered; either the diol *IX* exists for some reason in a rotamer in which the distance O—O is actually as high as about 3.7 Å or this is a case, where even a crude relationship between $\Delta\nu$ values and the distance of the interacting groups does not hold.

EXPERIMENTAL

The infrared spectra were measured on a Perkin-Elmer 621 spectrometer in Infracil cells of 20 mm thickness. Amino alcohols and N,N-dimethylamino alcohols were measured in tetrachloroethylene, other compounds in tetrachloromethane solutions. The concentration of the solutions was about $5 \cdot 10^{-3}\text{ mol} \cdot \text{l}^{-1}$.

TABLE III

Physical Constants and Analytical Values of Hydrazides and Urethanes, Corresponding to the Amino Alcohols *II-IV*

Compound ^a	M.p., °C (solvent)	Yield %	Found		
			% C	% H	% N
Hydrazides ^b					
<i>II</i>	261—264 (dec) (methanol)	90	62.81	8.66	13.34
<i>III</i>	154—156 (dec) (methanol)	98	62.53	8.62	13.32
<i>IV</i>	171—173 (methanol)	98	62.76	8.71	13.23
Urethanes					
<i>II</i> ^c	199—201 (ethanol)	85	68.21	7.61	7.09
<i>III</i> ^d	112—113 (methylcyclohexane)	80	65.05	8.72	6.08
<i>IV</i>	^e	88		^e	

^a The number given is that of the corresponding amino alcohol. ^b For $\text{C}_{11}\text{H}_{18}\text{N}_2\text{O}_2$ (210.2) calculated: 62.83% C, 8.63% H, 13.32% N. ^c Cyclic urethane; for $\text{C}_{11}\text{H}_{15}\text{NO}_2$ (193.2) calculated: 68.37% C, 7.82% H, 7.25% N. ^d For $\text{C}_{13}\text{H}_{21}\text{NO}_3$ (239.3) calculated: 65.25% C, 8.84% H, 5.85% N. ^e Isolated as an oil giving a single spot on thin layer chromatogram. The crude compound was directly hydrolysed to the amino alcohol *IVa*.

Curtius Degradation of Hydroxy Esters VI–VIII

A mixture of the corresponding hydroxy ester (2.0 g, 9.4 mmol) and 100% hydrazine hydrate (2.5 ml) in ethanol (6 ml) was heated in an ampoule for 10 hours to 100°C. The reaction mixture was taken down *in vacuo* and the hydrazide was purified by crystallization. For analyses and physical constants *cf.* Table III.

To a solution of the hydrazide (2.0 g, 9.4 mmol) in 0.935M-HCl (16 ml) a solution of sodium nitrite (1.04 g; 15 mmol) in water (10 ml) was added dropwise at +3°C under stirring which was continued for another 10 min. The cold reaction mixture was extracted with ether, washed with sodium hydrogen carbonate and dried. The dried solution was combined with 80 ml of ethanol, the ether was distilled off and the residue refluxed for 1 hour. Evaporation of the solvent afforded the corresponding urethane (Table III). The urethane (2.0 g, 8.4 mmol) was hydrolysed by boiling with a solution of KOH (4.5 g) in ethanol (30 ml) and water (10 ml). The usual isolation procedure afforded the amino alcohol (Table IV).

TABLE IV

Physical Constants, Yields and Analytical Data of the Amino Alcohols Ia–IVa and their N,N-Dimethyl Derivatives Ib–IVb

Compound	M.p., °C solvent	Yield %	Found		
			% C	% H	% N
Amino alcohols ^a					
Ia	125–128 (ligroin)	73	71.82	10.22	8.44
IIa	150.5–151 (ligroin)	90	71.83	10.23	8.55
IIIa	146–148 (ligroin)	70	71.57	10.17	8.37
IVa	195–200 (ethyl acetate)	55	72.22	10.32	8.45
N,N-Dimethylamino alcohols ^{b,c}					
Ib	38–39	69 ^d	73.87	11.01	7.13
IIb	44.5–45.5	85 ^d	73.58	11.00	7.27
IIIb	70–72	63	73.85	11.01	7.04
IVb	102–103	50	74.12	10.79	6.88

^a For C₁₀H₁₇NO (157.3) calculated: 71.81% C, 10.25% H, 8.37% N. ^b The compounds were distilled or sublimed *in vacuo*; they were homogeneous according to gas-liquid chromatography.

^c For C₁₂H₂₁NO (195.3) calculated: 73.79% C, 10.84% H, 7.17% N. ^d After reduction of the corresponding oxazolidine with lithium aluminium hydride.

exo-4-Hydroxy-*endo*-5-amino(*r*-1)tricyclo[4,4,0,0^{3,8}]decane (*IVa*)

A solution of 4,5-epoxytricyclo[4,4,0,0^{3,8}]decane (*XII*) (180 mg, 1.2 mmol) and a trace of ammonium chloride in 80% aqueous ethanol (10 ml) saturated with ammonia at -10°C was heated in an autoclave to 110°C for 8 hours. The usual work-up procedure followed by sublimation and crystallisation from ethyl acetate afforded 90 mg (45%) of product, identical with the amino alcohol prepared from the hydroxy ester *VIII*.

endo-4-Hydroxy-5-oximino(*r*-1)tricyclo[4,4,0,0^{3,8}]decane (*V*)

This compound was prepared in 61% yield from 4-hydroxytricyclo[4,4,0,0^{3,8}]decan-5-one by the usual treatment with hydroxylamine followed by two crystallisations from methanol; m.p. $166-167^{\circ}\text{C}$. For $\text{C}_{10}\text{H}_{15}\text{NO}_2$ (181.3) calculated: 66.27% C, 8.34% H, 7.73% N; found: 66.16% C, 8.26% H, 8.02% N.

endo-5-Amino-*endo*-4-hydroxy(*r*-1)tricyclo[4,4,0,0^{3,8}]decane (*Ia*)

Hydrogenation of the oxime from the preceding experiment (950 mg) in acetic acid (15 ml) over platinum oxide (110 mg) afforded *Ia* which on two crystallisations from ligroin had a constant melting point at $125-128^{\circ}\text{C}$. Yield 640 mg (73%). For $\text{C}_{10}\text{H}_{17}\text{NO}$ (157.3) calculated: 71.81% C, 10.25% H, 8.37% N; found: 71.82% C, 10.22% H, 8.44% N.

Preparation of Dimethylamino Alcohols *Ib-IVb*

The amino alcohols *Ia-IVa* were methylated by the standard Clarke-Eschweiler procedure and the physical constants of products are given in Table IV. The methylation product of the *cis*-isomers *Ia* and *Ila* was shown by gas-liquid chromatographic analysis to contain about 100% and 75%, respectively, of the corresponding oxazolidines *XIII* and *XIV* (molecular peak 193, absence of OH band in IR-spectrum). The crude methylation product was therefore reduced with lithium aluminium hydride and the product which was the pure N,N-dimethylamino alcohol, was isolated in the usual manner.

Determination of ΔH of the Equilibrium between Free and Bonded Hydroxyl in *IIIa*

The spectra of *IIIa* were taken at 6 temperatures and the hydroxyl bands separated by computer²³. From the plot of $\ln(B_b/B_f)$ against $1/T$ where B_b and B_f are the respective integrated intensities of the bonded and free hydroxyl band and T is absolute temperature, the value of ΔH was found using the least squares method. Following intensities were measured (temperature; B_b, B_f): 40.3°C : 939, 1145; 54.3°C : 884, 1158; 62.7°C : 870, 1218; 71.0°C : 828, 1199; 82.7°C : 740, 1192; 89.5°C : 717, 1204. The measurements were done in a 2 cm cell in tetrachloroethylene.

We are indebted to Dr A. Vitek for carrying out the computer separation of the infrared bands.

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