

CONFORMATION OF DIMETHYLAMINOETHANOL, ITS METHYL ETHER AND OF THE CORRESPONDING TRIMETHYLAMMONIUM IODIDES. NMR AND VIBRATIONAL SPECTRA

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By analysis of fully coupled ^{13}C NMR spectra and of ^1H NMR spectra of dimethylaminoethanol, its methyl ether, and of the corresponding trimethylammonium iodides, populations of isomers generated by rotation about the bonds $\text{N}-\text{CH}_2$, CH_2-CH_2 , and CH_2-O in these compounds in solution were determined. By analysis of Raman and infrared spectra of these compounds in the solid and liquid states it was found that in the crystalline state these compounds form structures with parallel $\text{N}-\text{CH}_3$ and $\text{O}-\text{CH}_2$ bonds, which are also preferred in the liquid state.

Information on the conformations of tertiary dimethylamines is rather scarce. The conformation of dimethylethylamine was investigated by vibrational spectra¹. In agreement with the results of ultrasonic relaxations in triethylamine^{2,3} it was found that by rotation around the $\text{C}-\text{N}$ bond in the liquid state, structures with *gauche* orientation of the ethyl group with respect to the free electron pair are preferentially generated. Besides these, structures with *trans*-orientation of the ethyl group with respect to the free electron pair also appear in the liquid state. For 2-hydroxyethyltrimethylammonium chloride $(\text{CH}_3)_3\text{N}^{(+)}\text{C}_2\text{H}_4\text{OH}.\text{Cl}^{(-)}$, in the crystalline state, the structure shown in Fig. 1 was found by X-ray analysis^{4,5}.

In order to determine which conformations are present in tertiary dimethylamines containing an ethoxy group, and how this structure is affected by the formation of quaternary iodides, the vibrational and NMR spectra of the following compounds were measured and interpreted: $(\text{CH}_3)_2\text{NC}_2\text{H}_5$ (I), $(\text{CH}_3)_2\text{NC}_2\text{H}_4\text{OH}$ (II), $(\text{CH}_3)_2.\text{NC}_2\text{H}_4\text{OCH}_3$ (III), $(\text{CH}_3)_3\text{N}^{(+)}\text{C}_2\text{H}_5.\text{I}^{(-)}$ (IV), $(\text{CH}_3)_3\text{N}^{(+)}\text{C}_2\text{H}_4\text{OH}.\text{I}^{(-)}$ (V), and $(\text{CH}_3)_3\text{N}^{(+)}\text{C}_2\text{H}_4\text{OCH}_3.\text{I}^{(-)}$ (VI). Our study of these compounds was prompted by the wish to investigate the conformations of poly(2-dimethylaminoethyl methacrylate) and of poly(2-methacryloyloxyethyltrimethylammonium iodide). N,N-Dimethylethylamine, with the corresponding quaternary iodide, was studied as the simplest tertiary amine forming isomers by rotation about the $\text{C}-\text{N}$ bond.

EXPERIMENTAL

Compounds

N,N-Dimethylethylamine (*I*), *p.a.* (Fluka), was used without further purification, purity 99.6% by GC. 2-Dimethylaminoethanol (*II*), a product of Fluka, was vacuum distilled, resulting purity 99.96% by GC. Methyl 2-dimethylaminoethyl ether (*III*) was prepared by a series of reactions from 2-methoxyethanol, transformed to methyl 2-chloroethyl ether by thionyl chloride. By reaction with sodium iodide in acetone this compound yielded⁶ methyl 2-iodoethyl ether, which gave the product by reaction with an ethanol solution of dimethylamine⁷; purity of product 99.89% by GC. Trimethylethylammonium iodide (*IV*) was prepared by reaction of *I* with methyl iodide in benzene solution. Trimethyl-2-hydroxyethylammonium iodide (*V*) was prepared by reaction of methyl iodide with 2-dimethylaminoethanol in ethanol. Trimethyl-2-methoxyethylammonium iodide (*VI*) was prepared by reaction of methyl 2-iodoethyl ether with trimethylamine in ethanol and repeated recrystallization of the product from ethanol.

Measurements of Spectra

¹H NMR spectra were measured on a CW NMR spectrometer PS 100 (JEOL) at 100 MHz and on the pulse NMR spectrometer XL-200 (Varian) at 200 MHz. Compounds *II*, *III*, *V*, and *VI* were measured as 10 and 5% solutions (w/v) in (²H₆)-DMSO at 295 and 353 K. The quaternary salts *V* and *VI* were also measured as 10% solutions in ²H₂O at 295 and 353 K. The amines *I* and *III* were measured as 10% solutions in C²HCl₃ in the temperature range 210–330 K. HMDS was used as internal standard in DMSO and C²HCl₃, DSS in ²H₂O solutions.

¹³C NMR spectra were measured on the spectrometer XL-200 (Varian) at 50 MHz, with a digital resolution of 0.156 Hz, with a pulse repetition time 5.2 s, in the gated decoupling mode preserving full coupling with NOE. Resolution enhancement by exponential weighting and apodization was used to achieve resolution better than 1 Hz in fully coupled ¹³C NMR spectra. Compounds *I* and *III* were measured as 50% (v/v), compound *VI* as 24% (w/v) solutions in (²H₆)-DMSO.

Raman spectra were measured on the spectrometer Coderg LRDH-800 connected on-line with the multi-channel spectra analyzer TN-11 Tracor-Northern. Spectra were excited by the line 514.5 nm of the argon laser CR-3 (Coherent Radiation). The spectra were measured in the 90° arrangement and were accumulated from several scans. The low-temperature spectra were measured in a cell with an evacuated jacket.

Infrared spectra were measured on the spectrometer Perkin-Elmer 621 connected on-line with a multichannel analyzer TN-4 000 (Tracor Northern).

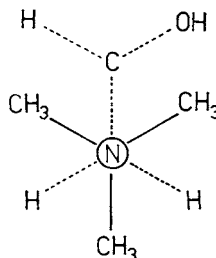


FIG. 1

Schematic representation of the conformation of $(\text{CH}_3)_3\text{N}^{(+)}\text{C}_2\text{H}_4\text{OH}.\text{Cl}^{(-)}$ in the crystalline state

Conformational Structures Considered

In the compounds studied in this work, conformers can be generated by rotation about the bonds $\text{N}-\text{CH}_2$, CH_2-CH_2 , and in the methylethers also about CH_2-O (Fig. 2). In previous studies of the conformation of tertiary amines¹⁻³ it was found that by rotation about the bond $\text{N}-\text{CH}_2$, only the forms shown in the staggered approximation in Fig. 2a are generated in measurable amounts. In compounds *I*, *II* and *III*, we designate these structures as t^{N} and g^{N} ; they can also be generated by inversion and rotation on the nitrogen atom. The way in which these structures are generated is not manifested in vibrational and NMR spectra. The population of t^{N} and g^{N} structures was followed by means of $^3J_{\text{CH}_3\text{NCH}_2}$ coupling in ^{13}C NMR spectra, and from temperature changes in vibrational spectra especially of compound *I*.

Conformations generated by rotation about the bond CH_2-CH_2 are shown in the staggered approximation in Fig. 2b. These forms we designate as *t* and *g*. The population of these conformations was followed by means of $^3J_{\text{HH}}$ coupling constants in ^1H NMR spectra by analysis of the NCH_2 (sometimes also OCH_2) multiplets in terms of AA' (or $\text{AA}'\text{BB}'$) systems and from temperature changes of vibrational spectra. In our notation the structure shown in Fig. 1 is designated as *g*.

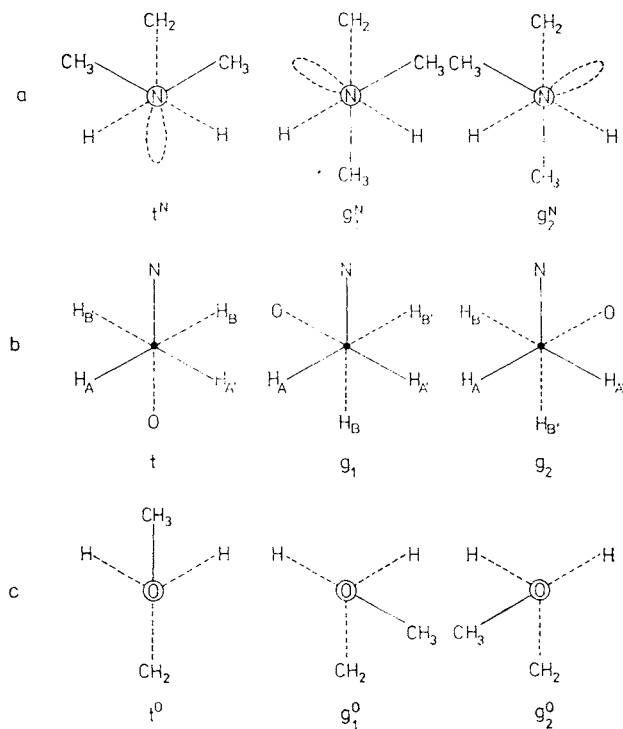


FIG. 2

Isomers of the studied compounds generated by rotation about the bond $\text{N}-\text{CH}_2$ (a); CH_2-CH_2 (b); CH_2-O (c)

In analogy to other methyl ethers⁸ we have assumed that also in compounds *III* and *VI*, conformers can be generated by rotation about the bond $\text{CH}_2\text{—O}$; these we have designated as *t*⁰ and *g*⁰ (Fig. 2c). The structures generated by rotation about this bond were followed by means of the ${}^3J_{\text{CH}_3\text{OCH}_2}$ coupling constants obtained by analysis of ${}^{13}\text{C}$ NMR spectra.

RESULTS AND DISCUSSION

NMR SPECTRA

The chemical shifts in ${}^1\text{H}$ NMR spectra are summarized in Table I. The ${}^1\text{H}$ NMR spectra of compounds *II* and *V* are shown in Fig. 3 and 4, the ${}^{13}\text{C}$ NMR spectrum of compound *III* is shown in Fig. 5.

Conformational Structure on Bond C—N

Generation of conformers by rotation about the bond C—N was studied by means of the fine structure of the NCH_3 carbon band in the fully coupled ${}^{13}\text{C}$ NMR spectra of compounds *I* and *III* dissolved in ${}^2\text{H}_6\text{—DMSO}$. By ${}^3J_{\text{CH}_3\text{NCH}_3}$ and ${}^3J_{\text{CH}_3\text{NCH}_2}$ coupling, each component of the NCH_3 quartet is split into 4×3 lines corresponding to ${}^3J_{\text{CH}}$ values of 5.5 and 4.7 Hz in compound *III* and to 5.6 and 4.7 Hz in compound *I*. We assume that in coupling through the amine nitrogen, the dependence of ${}^3J_{\text{CH}}$ on dihedral angle is approximately given, similarly as in analogous coupling through carbon^{9,10}, by the relation ${}^3J_{\text{CH}} = A \cos^2 \theta$, where θ is the dihedral angle between the bonds $\text{CH}_3\text{—N}$ and NC—H , carrying the interacting carbon and hydrogen nuclei, and the expression $\cos^2 \theta$ is averaged over all equivalent positions following from the symmetry of the molecule. From the value ${}^3J_{\text{CH}_3\text{NCH}_3}$ in compounds *I* and *III* (5.6 and 5.5), the value of A can be estimated as equal to 11 Hz.

TABLE I

${}^1\text{H}$ NMR chemical shifts, δ (ppm from HMDS or DSS), 22°C, 100 MHz

Solvent	N—CH ₃ N—CH ₂ O—CH ₂ O—CH ₃				Solvent	N—CH ₃ N—CH ₂ O—CH ₂ O—CH ₃			
	Compound <i>II</i>					Compound <i>V</i>			
C^2HCl_3	2.18	2.39	3.53	—	DMSO	3.08	3.37	3.77	—
DMSO	2.08	2.24	3.40	—	${}^2\text{H}_2\text{O}$	3.20	3.52	4.04	—
	Compound <i>III</i>					Compound <i>VI</i>			
C^2HCl_3	2.20	2.40	3.40	3.30	DMSO	3.07	3.49	3.70	3.25
DMSO	2.07	2.31	3.32	3.16	${}^2\text{H}_2\text{O}$	3.70	3.60	3.90	3.49

The similarity of the values of ${}^3J_{\text{CH}_3\text{NCH}_2}$ in compounds *I* and *III* (4.5 and 4.7, resp.) indicates that the conformational forms generated by rotation about the bond N—C in compounds *I* and *III* are very similar. For the coupling pathway ${}^3J_{\text{CCCH}}$, substitution by carbon in the γ position decreases the value of *A* approximately^{11,12}

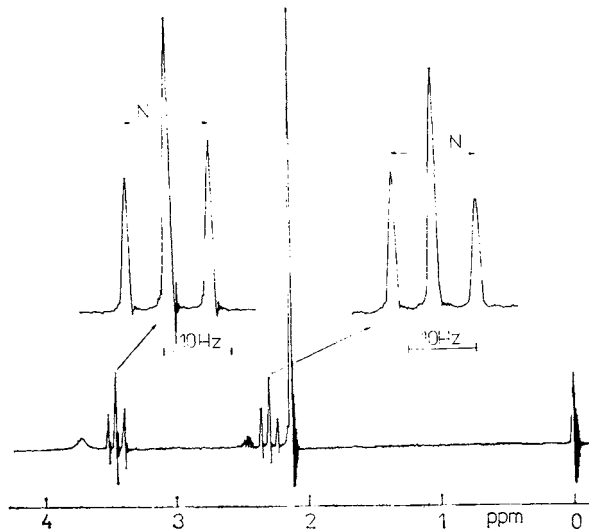


FIG. 3

100 MHz ${}^1\text{H}$ NMR spectrum of compound *II*, 10% (w/v) in (${}^2\text{H}_6$)-DMSO

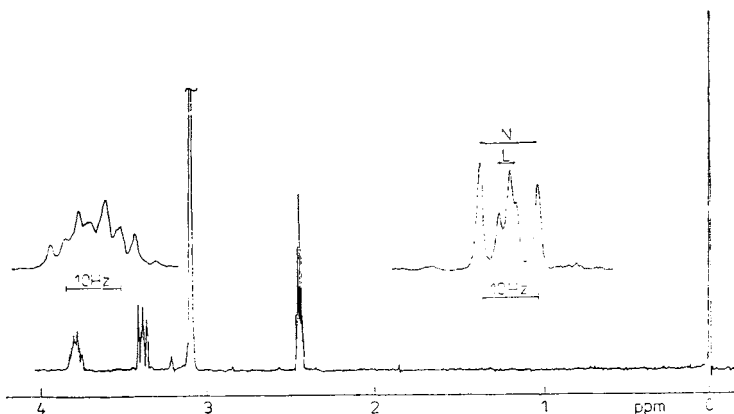


FIG. 4

200 MHz ${}^1\text{H}$ NMR spectrum of compound *V*, 5% (w/v) in (${}^2\text{H}_6$)-DMSO

by 2 Hz. Assuming that the substitution increments are similar even for the coupling pathway ${}^3J_{\text{CNCH}_2}$, we obtain for ${}^3J_{\text{CH}_3\text{NCH}_2}$ in compounds *III* and *I*, $A = 9$. Using this estimated value of A , the experimental values of ${}^3J_{\text{CH}_3\text{NCH}_2}$ in compounds *I* and *III* correspond to $\overline{\cos^2 \theta} = 0.5$ and 0.52 , respectively.

The conformation g^N corresponds to the value $\overline{\cos^2 \theta} = 0.4375$, and the conformation t^N to the value $\overline{\cos^2 \theta} = 0.6125$. The values of $\overline{\cos^2 \theta}$ calculated for the compounds *I* and *III* are in agreement with the notion that in the liquid state these compounds form g^N and t^N conformations, with predominance of g^N .

Conformation on Bond $\text{CH}_2\text{—CH}_2$

Conformations generated by rotation about the bond $\text{CH}_2\text{—CH}_2$ were followed by analysis of the NCH_2 and OCH_2 bands in ${}^1\text{H}$ NMR spectra. Because of the symmetry of the studied molecules, the x_{g1} and x_{g2} populations must be equal, and the NCH_2 and OCH_2 bands in 100 MHz ${}^1\text{H}$ NMR spectra of the amines and in 200 MHz ${}^1\text{H}$ NMR spectra of the quaternary iodides appear as triplets or more complicated multiplets corresponding to the $\text{AA}'\text{XX}'$ system¹³. The 100 MHz NMR spectra of the quaternary iodides exhibit multiplets corresponding to $\text{AA}'\text{BB}'$ systems¹³. In the spectra of quaternary iodides the band of the OCH_2 group exhibits further splitting by $\text{H—C—C—}{}^{14}\text{N}^+$ coupling. ${}^{14}\text{N}^+$ coupling is not manifested on N^+CH_2

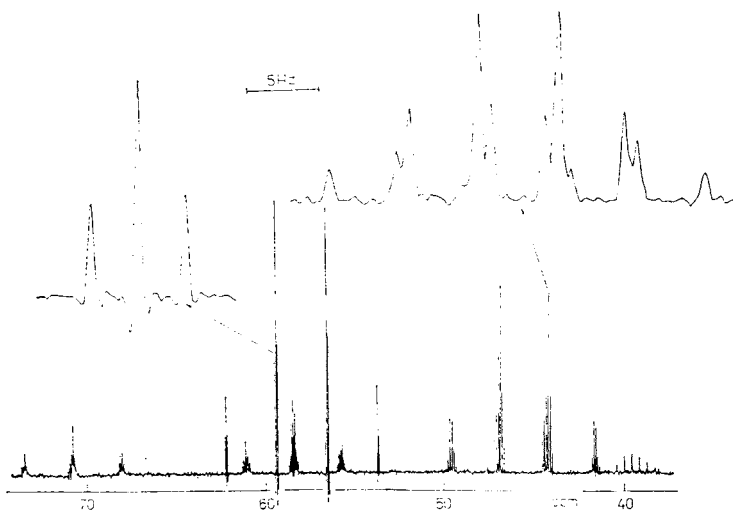


FIG. 5
50 MHz ${}^{13}\text{C}$ NMR spectrum of compound *III*, 1 : 1 (v/v) in $({}^2\text{H}_6)$ -DMSO, fully coupled, with NOE, resolution enhancement by exponential weighting and apodization

and N^+CH_3 bands, in agreement with the literature¹⁴. Therefore we analyzed mainly the NCH_2 bands.

In the system $AA'XX'$ the spacing of the outer triplet (or multiplet) components is equal to the value of the parameter $D = J_{AX} + J_{AX'}$ (Figs 3, 4). In systems where $J_{AA} - J_{XX} = 0$ and $J_{AA'} + J_{XX'} = K \gg L = J_{AX} - J_{AX'}$, $|L|$ is equal to the spacing of the weak lines flanking the central signal (Fig. 4). In systems with somewhat stronger coupling and in those cases where the above approximations are not rigorously fulfilled, several unresolved lines occur in the band centre, and this is manifested by a broadening of the central line.

The populations of the conformers on bond C—C and the values of the vicinal coupling constants are related as follows:

$$J_{AX} = x_t J_T + 2x_g J_G$$

$$J_{AX'} = x_t J_G + x_g (J_T + J_G).$$

As $x_t + 2x_g = 1$, it holds

$$N = J_{AX} + J_{AX'} = (J_T + J_G) - x_g (J_T - J_G); \quad x_g = \frac{(J_T + J_G) - N}{J_T - J_G}$$

$$L = J_{AX} - J_{AX'} = (J_T - J_G) - 3x_g (J_T - J_G);$$

$$x_g = \frac{(J_T - J_G) - L}{3(J_T - J_G)},$$

where the parameters J_T , J_G correspond to the value of ${}^3J_{HH}$ for the dihedral angles 180° and 60° , respectively, between the bonds carrying the coupled protons.

In C^2HCl_3 solution of compound *II*, the value of N varies from 11.1 Hz at 333 K to 10.0 Hz at 216 K, in compound *III* from 11.5 Hz to 10.2 Hz in the same temperature range. In compound *II* the width of the central line increases with decreasing temperature, and a poorly resolved fine structure gradually appears. Compound *III* behaves similarly, but the broadening of the central line is less well pronounced.

According to the above relations, irrespective of the values of the parameters J_T , J_G , the decrease of N with decreasing temperature indicates an increase of the population x_g . A simultaneous increase of x_g and $|L|$ indicates $L < 0$, $J_{AX'} > J_{AX}$ and $x_g > 1/3$; $x_t < 1/3$. Irrespective of the values of the parameters J_T , J_G , measurements of the temperature dependence of 1H NMR spectra of the two amines indicate that (i) the *g* forms predominate even at room temperature, and the content of the *t* form decreases with decreasing temperature; (ii) the population x_t is lower in compound *II* than in compound *III*, where x_t approaches the value $1/3$ at room temperature.

For the values¹⁵ $J_T + J_G = 13.5$ and $J_T - J_G = 8.1$, the values x_t for compound *II* at 333 and 216 K are 0.41 and 0.13, respectively, and for compound *III* at the same two temperatures, x_t is 0.5 and 0.18, respectively. In view of the preceding qualitative considerations, these x_t values are to be regarded as the maximum possible. The condition $x_t < 1/3$ roughly conforms with the parameter values $J_T + J_G = 14.3$ and $J_T - J_G = 8.6$ which yield at 333 K for compounds *II* and *III* x_t 0.26 and 0.35, respectively. In $^2\text{H}_6$ -DMSO solutions of the two amines both at elevated and at room temperature, the broadening of the central line is not apparent, indicating that even in this solvent $x_t \cong 1/3$.

For the quaternary iodides, the compounds *V* and *VI*, the value of N was determined in $^2\text{H}_6$ -DMSO solution from spectra measured at 200 MHz. It was found that the value of N in this solvent does not change between 295 and 353 K and is equal to 10.3 and 9.6 Hz, for *V* and *VI*, respectively. These values indicate a small content of form *t* in compounds *V* and *VI*. With $J_T + J_G = 13.5$ and $J_T - J_G = 8.1$ the value of N indicates for *V* and *VI* x_t 0.21 and 0.04, respectively; with $J_T + J_G = 14.3$ and $J_T - J_G = 8.6$, x_t is 0.07 and 0, respectively.

^1H NMR spectra of the two quaternary iodides measured in $^2\text{H}_6$ -DMSO at 200 MHz exhibit a resolved structure in the centre of the multiplet, corresponding to $|L| = 3$ Hz for *V* and $|L| = 4$ Hz for *VI*. These values do not measurably change in the temperature range 295–353 K. For negative L values, which follow from the measured magnitude of $|L|$ and the above relations, the content of x_t in compounds *V* and *VI* is equal to 0.09 and 0.01, respectively, with $J_T - J_G = 8.1$, and to 0.10 and 0.02 with $J_T - J_G = 8.6$.

The solutions of the quaternary iodides in $^2\text{H}_2\text{O}$ were measured only at 100 MHz, and the respective proton CH_2 bands therefore could not be analyzed in terms of an AA'XX' system (small chemical shift difference of OCH_2 and NCH_2 bands, see Table I). Nevertheless, these 100 MHz spectra exhibit structure of the central line of the triplet which is very similar to the structure of this line in 100 MHz spectra measured in ($^2\text{H}_6$)-DMSO solution, indicating similar conformation in $^2\text{H}_2\text{O}$ and ($^2\text{H}_6$)-DMSO.

Conformational Structure on the Bond O—C

For both studied ethers dissolved in ($^2\text{H}_6$)-DMSO, the population of rotational isomers on the bond O—C at room temperature was determined from the vicinal coupling constant $^3J_{\text{CH}_3\text{OCH}_3}$ by a procedure analogous to our previous publication on the conformation of a series of ethers. In fully coupled ^{13}C NMR spectra, the components of the OCH_3 quartet appear as triplets with the spacing of the outer triplet components equal to 6.6 Hz with *III* and to 6.0 Hz with *VI*. These values are very similar to those which we have found in the simple ethers ($\text{CH}_3\text{OCH}_2\text{CH}_3$ 6.5;

$\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)_2$ 6:3). Therefore we may conclude that also in the presently studied ethers form *t* predominates, with $x_t = 0.8$ for *III* and $x_t = 0.9$ for *VI*.

VIBRATIONAL SPECTRA

We have measured the Raman spectra of all the studied amines, compounds *I*, *II* and *III*, in liquid and in crystalline state, and of the quaternary iodides, compounds *IV*, *V* and *VI*, in the crystalline state and in H_2O solution. With compounds *II* and *III*, we could even measure Raman spectra in the solid glassy state. Infrared spectra of the amines could only be measured in the liquid state. In infrared cells at tempera-

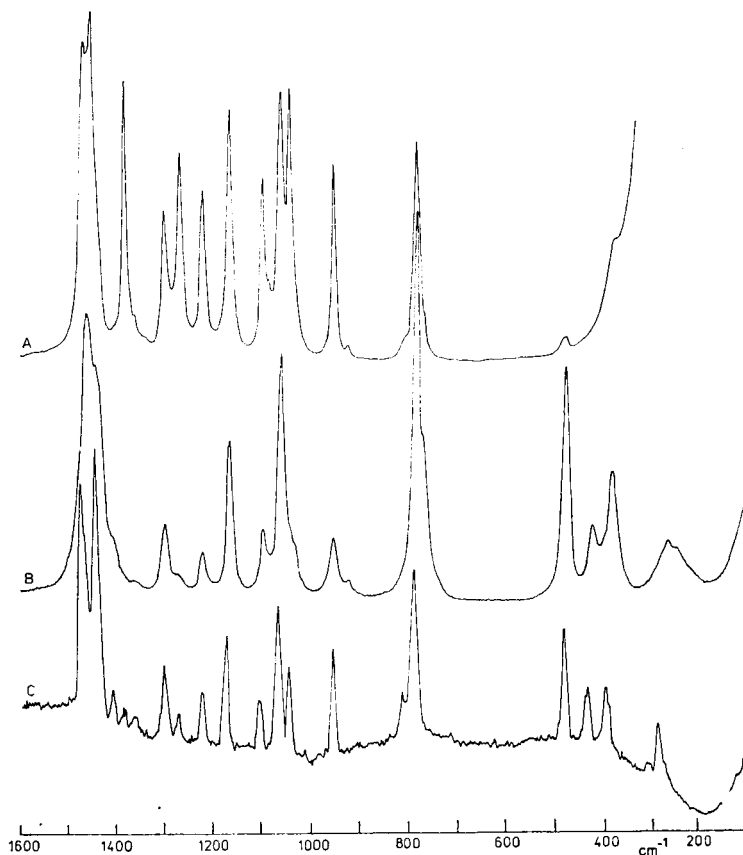


FIG. 6

Infrared (A) and Raman (B, C) spectra of compound *I*. A, B liquid; C crystal

ture below the melting point of the samples, the studied amines could not be crystallized. Infrared spectra of the iodides were measured in the crystalline state. The spectra are shown in Figs 6–11. Upon transition from liquid to crystalline state, band shifts and band disappearance are observed with the studied compounds. In agreement with the symmetry of the compounds, all bands observable in the Raman spectra of liquid samples are also observable in infrared spectra of these samples. Raman spectra were found to be better suited for conformational analysis, because complete spectra in the liquid and crystalline states could be obtained with all compounds, and the spectra of the solid glassy state with *II* and *III*. The assignment of the conformationally sensitive bands found in Raman spectra was verified by the measurement of the temperature dependences of infrared spectra.

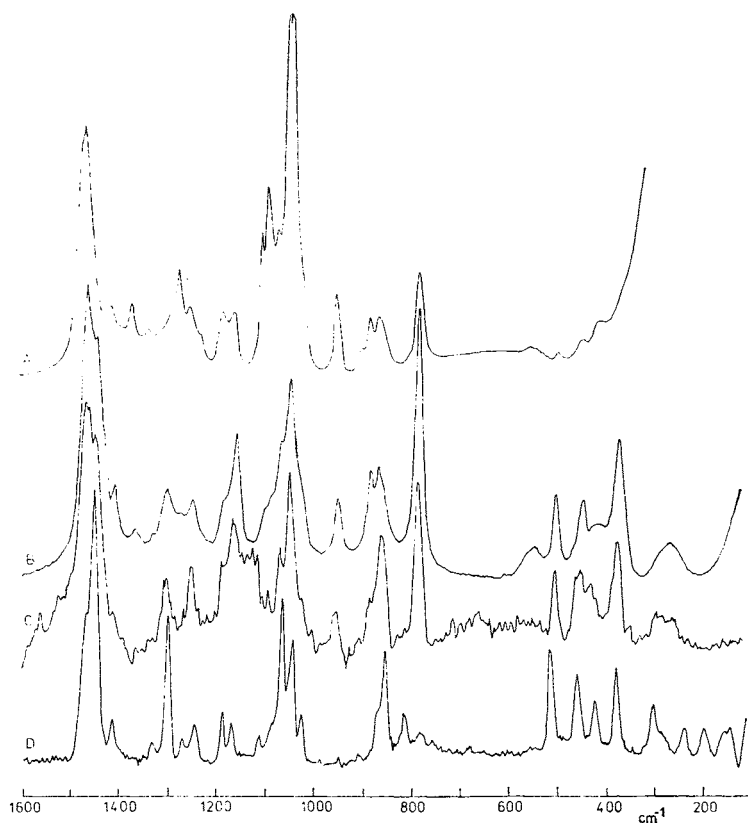


FIG. 7

Infrared (A) and Raman (B, C, D) spectra of compound *II*. A, B liquid; C glass; D crystal

Raman Spectra of Quaternary Iodides

In Raman spectra, the studied quaternary iodides exhibit a strong band in the range about 715 cm^{-1} . Upon dissolution in water, Raman spectra of compounds *V* and *VI* exhibit a new weak band at 764 and 760 cm^{-1} , respectively. As this band appears in solutions of *V* and *VI*, and its intensity in relation to the intensity of the band

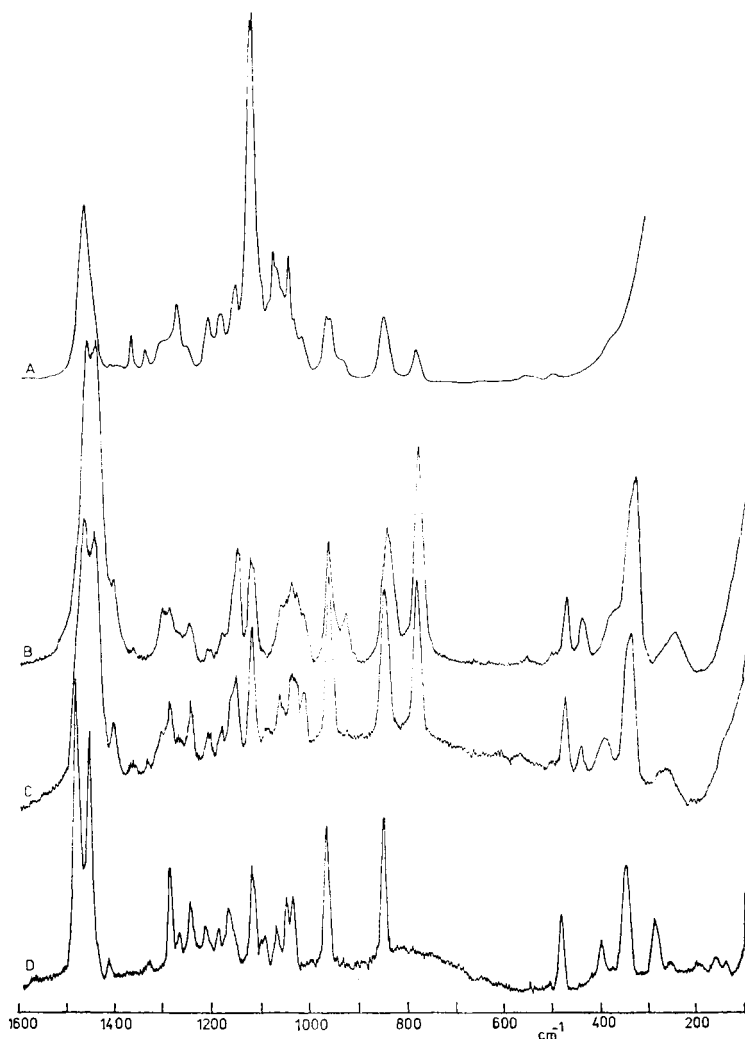


FIG. 8

Infrared (A) and Raman (B, C, D) spectra of compound *III*, A, B liquid; C glass; D crystal

at 715 cm^{-1} corresponds to the population of t forms as determined from ^1H NMR spectra, we assume that it is characteristic of the t conformations in compounds V and VI. The relative intensity of this band with respect to the band at 715 cm^{-1} is about twice higher in compound V than in compound VI; this is in agreement with the low content of t forms as determined from NMR spectra analysis. We have not succeeded in identifying bands connected with the formation of conformational isomers generated by rotation about the bond C—O in compounds V and VI.

Vibrational Spectra of Amines

In the Raman spectra of compound I in the liquid state, a weak band at 770 cm^{-1} was detected¹ at the base of the strong band at 788 cm^{-1} ; this weak band was assigned to the t^N conformation of I. In our studies we made use of a better resolved pair at 953 and 924 cm^{-1} . The band at 953 cm^{-1} which appears both in the crystal-

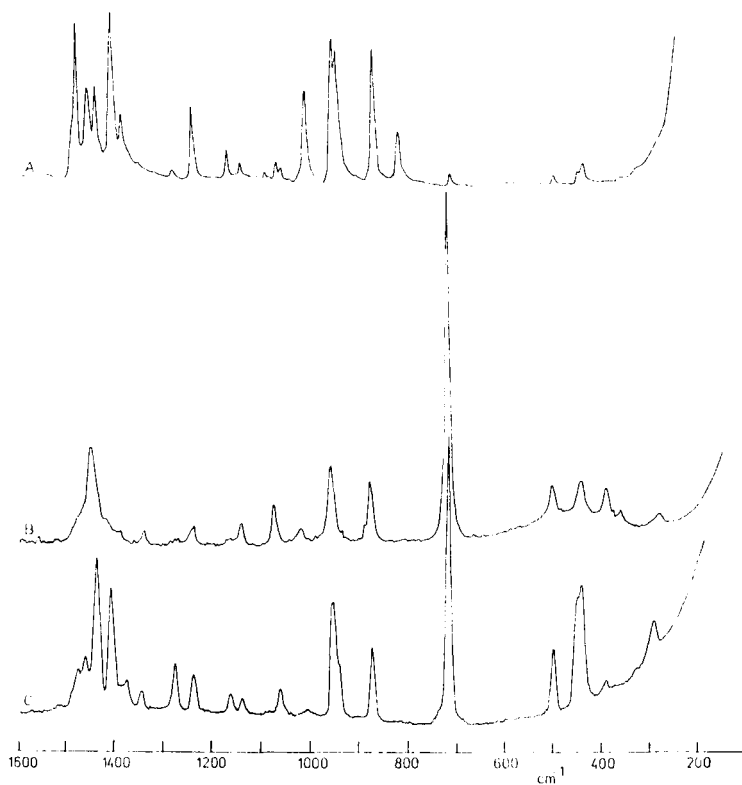


FIG. 9

Infrared (A) and Raman (B, C) spectra of compound IV. A, C crystal; B solution in H_2O

line and in the liquid state we assigned to the g^N conformation, and the band appearing only in the liquid state at 924 cm^{-1} to the t^N conformation. Measurements of the temperature dependence of this band pair revealed that this band disappears at 153 K , where compound *I* is still liquid; the enthalpy difference between the forms g^N and t^N was determined as $\Delta H = 5\text{ kJ mole}^{-1}$.

Upon cooling of compounds *II* and *III* to the glassy state, the intensity of some bands of the liquid state decreases, and some bands disappear completely. The former disappear completely in Raman spectra of the crystalline samples. This indicates that at least three conformers are present in the liquid state. This is best demonstrated in the range $700\text{--}1\,000\text{ cm}^{-1}$ in Raman spectra. The Raman spectrum of compound *III* in the liquid state exhibits 4 prominent bands at $784, 851, 931$ and

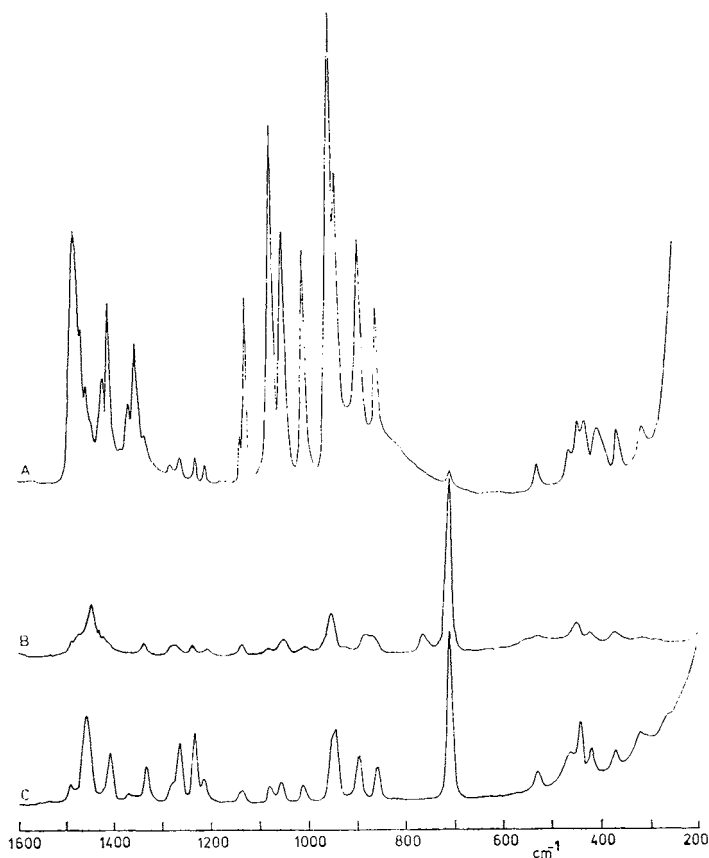


FIG. 10

Infrared (A) and Raman (B, C) spectra of compound *V*. A, C crystal; B solution in H_2O

968 cm^{-1} . In the glassy state the intensity of the band at 784 cm^{-1} decreases, and the band at 931 completely disappears. In the crystalline state, also the band at 784 cm^{-1} disappears, with the band at 848 cm^{-1} remaining as the strongest in this range. The situation is similar in the Raman spectra of compound *II*. In Raman spectra of liquid sample *II*, in the range 700 to 900 cm^{-1} , the band at 777 cm^{-1} is the strongest. The intensity of this band decreases in the glassy state, and it disappears completely in the crystalline state. In the crystalline sample, the band at 846 cm^{-1} is the strongest in this range, similarly as with compound *III*.

In Raman spectra of compound *I*, where conformational isomers can only be generated by rotation about the bond $\text{CH}_2\text{—N}$, rotamer formation is only manifested by weak bands at 770 and 924 cm^{-1} . Therefore we assume that the pronounced changes of strong bands in the range $750\text{—}950\text{ cm}^{-1}$ observed in measurements of the temperature dependence of Raman spectra of samples *II* and *III* are caused by the conformers generated by rotation about the bond $\text{CH}_2\text{—CH}_2$, the population

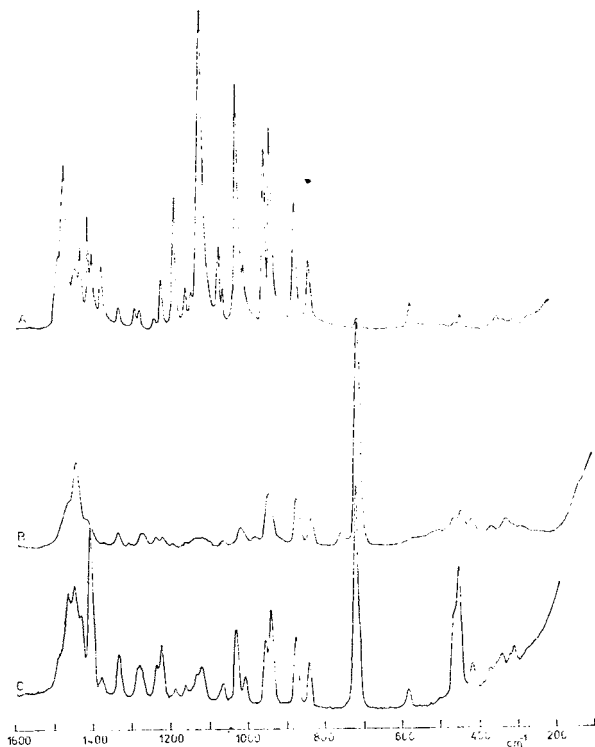


FIG. 11

Infrared (A) and Raman (B, C) spectra of compound *VI*. A, C crystal; B solution in H_2O

of which strongly changes with temperature according to ^1H NMR spectra. Based on ^1H NMR analysis we assume that the band at 777 cm^{-1} of compound *II*, and at 784 cm^{-1} of compound *III*, of intensity decreasing with decreasing temperature, is to be assigned to t conformations, and the band near to 850 cm^{-1} which is the strongest band in this range in the crystalline samples *II* and *III*, to g conformations. The band at 931 cm^{-1} which disappears in the Raman spectrum of *III* in the glassy state, is connected with the content of t^{N} or g^{O} conformations. As in compound *I* the t^{N} conformation practically disappears at 163 K, we assume that in compound *III* the band at 931 cm^{-1} is connected with this structure. According to NMR spectra, in the quaternary iodides (compounds *V* and *VI*) the content of t conformations is very small, indicating energetic preference for the g conformation with parallel orientation of $\text{N}-\text{CH}_3$ and $\text{O}-\text{CH}_2$ bonds (Fig. 1). The larger population of t forms in compounds *II* and *III* than in *V* and *VI* indicates that the g conformation with parallel $\text{N}-\text{CH}_3$ and $\text{O}-\text{CH}_2$ bonds is more favoured energetically than the conformation with the $\text{N}-\text{CH}_3$ bond parallel to the free electron pair. Therefore we assume that the Raman band at 850 cm^{-1} in compound *II* and *III* is to be assigned to the g conformation with parallel $\text{N}-\text{CH}_3$ and $\text{O}-\text{CH}_2$ bonds.

CONCLUSION

Measurements of vibrational spectra together with the analysis of NMR spectra indicate that in the crystalline state compound *I* is present in the form g^{N} , compound *II* in the form g^{Ng} , compound *III* in the form $g^{\text{Ngt}^{\text{O}}}$, compound *V* in the form g and compound *VI* in the form gt^{O} . The structure of compound *III* which can generate conformers by rotation about all the three considered bonds, is shown in Fig. 12; the structures of all the other compounds in the crystalline state can be derived from this figure. The above named conformations are the major forms even in the liquid state, where they are accompanied by t^{N} conformations in compounds *I*, *II*, and *III*, by g^{O} conformations generated by rotation about the bond CH_2-O in compounds *III* and *VI*, and by t conformations generated by rotation about the

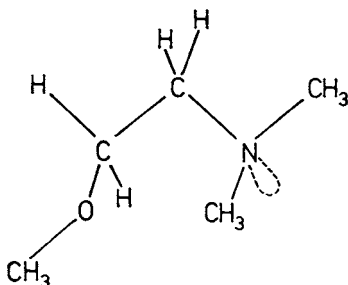


FIG. 12
Schematic representation of the structure of compound *III* in the crystalline state

CH₂—CH₂ bond in compounds *II*, *III*, *V*, and *VI*. In compounds *II* and *III* at room temperature the content of *t* conformations is about 30%, and in the *g* conformations, the form with parallel N—CH₃ and O—CH₂ bonds predominates.

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