ARCHIVES OF ACOUSTICS
11, 4 (1986)

DETERMINATION OF THE INFLUENCE OF LIQUID MOLECULE STRUCTURE ON ACOUSTIC ABSORPTION QUANTITY*

BOGUMIŁ LINDE, MAREK KOSMOL, ANTONI ŚLIWIŃSKI

Institute of Experimental Physics, University of Gdańsk
(ul. W. Stwosza 57, 80-952 Gdańsk)

This paper is concerned with the propagation mechanism of ultrasonic waves. It was aimed at the determination of relation the values of the absorption coefficient $(\alpha/f^2)_{rel}$ and the structure of liquid molecules. Such relation were observed in the course of investigations performed on cyclic compounds [1–4].

Introduction

Acoustic relaxation processes take place due to interactions between an ultrasonic wave and the environment in which it propagates. Effects accompanying the propagation of an ultrasonic wave and its interactions with molecules of the liquid medium, especially molecular relaxation due to energy exchange between the acoustic wave and the vibrational degrees of freedom (Kneser relaxation), constitute a certain class of these processes. Such relaxation has been observed in liquids with cyclic molecular structure. Although hitherto research has not been systematic, results published in literature show that relaxation effects are influenced by molecule structure.

Within this research a greater number of substances from similar structure groups was investigated and the interactions between the values of the relaxation coefficients $(\alpha/f^2)_{rel}$ and the molecule structure of these substances was determined.

Many authors (BERGMANN and JAENSCH [5], PARTHASARATHY [6], RAO [7], LAGEMANN [8], SCHAAFFS [9] and SETTE [10]) very accurately determined relations between the propagation velocity of ultrasonic waves and liquid molecule structure, but there are no systematic papers concerned with the relationship between the absorption coefficient α/f^2 and molecule structure. Only three aut-

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* Work performed within the framework of the problem MR. I. 24.

hors have classified liquids in relation to the attenuation quantity: Pinkerton [11] on the basis of the a_{exp}/a_{cl} ratio, Michajłow [12] dividing the frequency measuring range into five relaxation ranges, and Verma [13], who took into consideration the mechanism responsible for absorption. These approaches are not based on the dependences between sound attenuation and molecule structure. Szachparonow and Tunin [14] observed that in rigid molecules with active electrons π the absorption of ultrasounds, which is always caused by energy transition to vibrational degrees of freedom, is considerable and the relaxation time is about 10^{-10} s. This conclusion has been confirmed by investigations presented below.

On the basis of own investigations and data from literature, concerning ultrasound absorption in cyclic compounds, certain strict relations between $(\alpha/f^2)_{rel}$ and molecule structure of a given liquid can be established.

Research was performed on non-associated liquids without rotational isomers, in which structural relaxation processes do not occur, i.e. absorption of an ultrasonic wave mainly due to Kneser relaxation [15].

On the basis of the analysis of achieved results, investigated substances have been divided into five characteristic group according to: relations between $(\alpha/f^2)_{rel}$ and the number of substituents in molecules (groups I and II), the exchange of carbon atoms by nitrogen (group III), molecule enlargement caused by substituent exchanges (group IV) and changes caused by bond saturation in a ring (group V).

Apparatus

The amplitude absorption coefficient, α/f^2, of an ultrasonic wave was measured with the pulse method in two measuring set-ups covering frequency ranges from 10 to 180 MHz and from 400 to 1300 MHz.

A modernized ultrasonic spectrometer *US*-3 [3] was applied in the first range, while in the second range a system designed by Leźniew [17], which employs the method of non-resonance excitation of a lithium niobate monocrystal in a resonance chamber, was used.

The principle of operation of this system, presented in Fig. 1, is as follows; the two-channel pulse generator — *1* switches on the oscilloscope time base — *2*, the pulse generator — *4* and modulates generator signals — *3*. A pulse with a determined carrier frequency leaves the high frequency generator and enters the coaxial quarter-wave resonator — R_1 through the coupling loop — P_1. A quarter of the length of an electromagnetic wave is saved in the resonator cavity. The resonance frequency could be smoothly changed with a slidable tuner in a range from 400 to 1300 MHz. A 5 mm in radius and 15 mm in length lithium niobate crystal *I* was inserted in the center of the resonant cavity, so one end was within the range of the variable electric field. When the field in the resonator was excited by pulses, a pulse of mechanical vibrations was generated on the surface of the crystal, propagated along it and entered the investigated liquid [18]. (The R_1 resonator together with the transducer were attached to the mobile part of the cathetometer, moved with a $5 \cdot 10^{-7}$ m accuracy, in order to regulate the acoustic path in the liquid). After passing through the liquid, the acoustic pulse enters transducer *II*, where it is again changed into an electric pulse, which is fed into the input of the receiving amplifier *7* through resonator R_2 and coupling loop P_2 and then, sent directly to oscilloscope *2*.

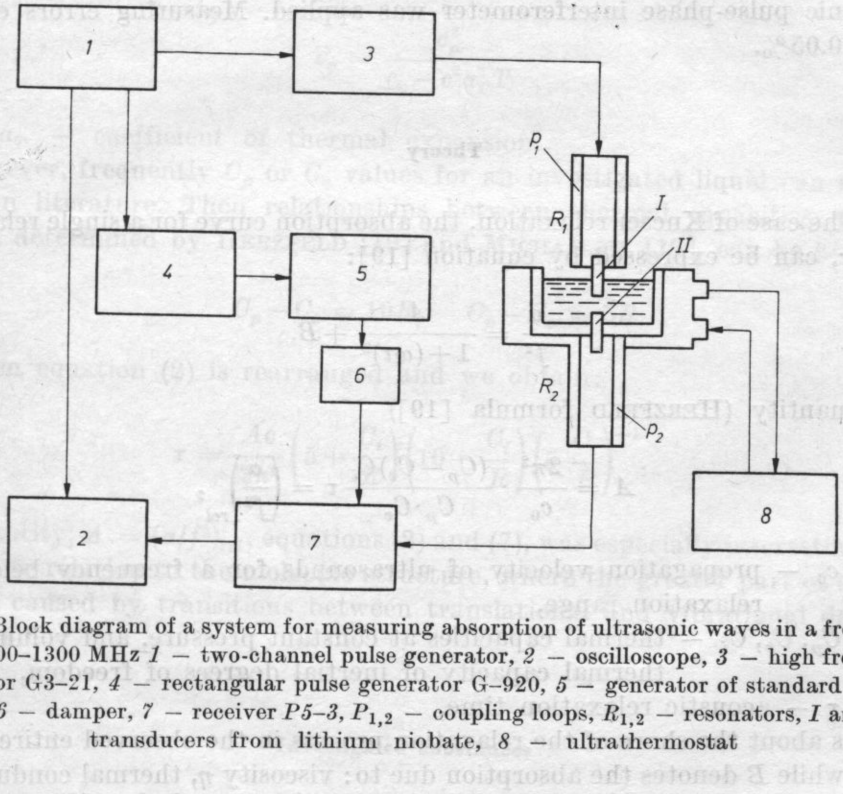


Fig. 1. Block diagram of a system for measuring absorption of ultrasonic waves in a frequency range 100–1300 MHz *1* – two-channel pulse generator, *2* – oscilloscope, *3* – high frequency generator G3–21, *4* – rectangular pulse generator G–920, *5* – generator of standard sygnals G4–44, *6* – damper, *7* – receiver *P5–3*, $P_{1,2}$ – coupling loops, $R_{1,2}$ – resonators, *I* and *II* – transducers from lithium niobate, *8* – ultrathermostat

The mentioned above pulse generator *4* (acts as a regulated delay line and cuts out the unnecessary initial part of the pulse, giving a more legible oscilloscope picture) switches on the calibrated pulse generator *5*. Generator *5* sends a pulse through a damper (regulated smoothly from 0 to 30 dB with a 0.1 dB accuracy) to oscilloscope *2*. This pulse is used in the absolute measurement of the amplitude absorption coefficient. Comparing amplitudes of two signals: ultrasonic, A_1, and calibrated, A_2, the value of the absorption coefficient, expressed in [s²/m], can be determined according to equation:

$$\frac{\alpha}{f^2} = \frac{\Delta A}{f^2 \Delta s \, 20 \log e}.$$

Every absorption measurement was repeated ten times for different lengths of the ultrasonic wave path in investigated liquids and, possibly, in various points of this path.

The temperature was stabilized with an *U-10* ultrathermostat with the accuracy of 0.1 K.

Estimated errors of determining the absorption coefficient are contained in a range from 3.5% for the frequency of 400 MHz to 5% for 1300 MHz.

Additional measurements of the propagation velocity of ultrasounds were performed in order to calculate classical absorption coefficients. An *UI-12* ultrasonic pulse-phase interferometer was applied. Measuring errors equaled about 0.05%.

Theory

In the case of Kneser relaxation, the absorption curve for a single relaxation time, τ, can be expressed by equation [19]:

$$\frac{\alpha}{f^2} = \frac{A}{1+(\omega\tau)^2} + B. \tag{1}$$

The quantity (Herzfeld formula [19])

$$A = \frac{2\pi^2}{c_0} \cdot \frac{(C_p - C_v)\,C_i}{C_p \cdot C_v}\,\tau = \left(\frac{\alpha}{f^2}\right)_{rel}, \tag{2}$$

where c_0 – propagation velocity of ultrasounds for a frequency below the relaxation range,

C_p, C_v, C_i – thermal capacities at constant pressure, and volume, and thermal capacity of inertial degrees of freedom,

τ – acoustic relaxation time,

informs about the share of the relaxation process in the observed entire absorption, while B denotes the absorption due to: viscosity η, thermal conductivity $\varkappa$, and possibly other relaxation processes with relaxation times considerably shorter than τ. Therefore, it represents the classic part of the absorption coefficient, determined by Stokes [20]:

$$B = \left(\frac{\alpha}{f^2}\right)_{kl} = \frac{8\pi^2}{3\varrho c^3}\eta, \tag{3}$$

where ϱ is the density.

Relaxation time, τ, can be determined knowing the A quantity, thermal capacities, C_p and C_v, and the frequencies of vibrational degrees of freedom in molecules, ν_i, which enable the calculation of C_i according to the Planck-Einstein formula [21]:

$$C_i = R \sum_i g_i \left(\frac{h\nu_i}{kT}\right)^2 \exp\left(-\frac{h\nu_i}{kT}\right)\left[1-\exp\left(-\frac{h\nu_i}{kT}\right)\right]^{-2}, \tag{4}$$

where: g_i — degree of degeneration, ν_i — frequency of the i vibration, h, k and T — Planck and Boltzman constants, and temperature.

If C_v is unknown, then the relation between the propagation velocity of an acoustic wave, c, and specific heats, c_p and c_v, [22], can be applied:

$$c_v = \frac{c_p^2}{c_p + c^2 \alpha_T^2 T} \tag{5}$$

where α_T — coefficient of thermal expansion.

However, frequently C_p or C_v values for an investigated liquid can not be found in literature. Then relationships between thermal capacities, C_p, C_v and C_i, determined by HERZFELD [19] and MICHAJŁOW [12], can be applied:

$$C_p - C_i \approx 10R, \quad C_p - C_v \approx 5R$$

and then equation (2) is rearranged and we obtain:

$$\tau = \frac{Ac}{2\pi^2}\left(5+\frac{C_i}{R}\right)\left(10+\frac{C_i}{R}\right)\left(5\ \frac{C_i}{R}\right)^{-1}. \tag{7}$$

The quantity, $A = (\alpha/f^2)_{rel}$, equations (2) and (7), was especially interesting due to its close relation to the molecule structure, where the greater part of absorption is caused by transitions between translational and vibrational degrees of freedom.

Investigated substances

42 aromatic and heterocyclic compounds were chosen for investigation. The necessary acoustical data for ten compounds can be found in literature, while as for the other 32 liquids — the authors performed required measurements.

Measurements proved that the entire research material can be divided into five groups according to relations between $(\alpha/f^2)_{rel}$ and the molecule structure:

Group I

Benzene, toluene, *p*-xylene, *o*-xylene, *m*-xylene, pseudoucumene, hemihexamethylbenzene.

Group II

Pyridine, α-picoline, β-picoline, γ-picoline, 3-4 lutidine, 2-4 lutidine, 2-5 lutidine, 3-5 lutidine, 2-6 lutidine, 2,4,6-collidine, 2,5,6-collidine, aniline, ethylaniline.

Group III

Benzene, pyridine, pyrimidine, naphthalene, quinoline.

Group IV

Toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, 3,4-lutidine, β-collidine, 2,5-lutidine, 2-methyl-5-ethylpyridine, toluene, acetophenone, toluene, benzyloamine, α-picoline, 2-ethylpyridine, γ-picoline, 4-ethylpyridine, naphthalene, bromonaphthalene, 2-methylnaphthalene.

Group V

Pyridine, piperdine, furane, tetrahydrofuran, pyrrole, pyrrolidine, naphthalene, decalin.

Picolines and xylenes, which were investigated first, were additionally purified, but it was stated that this process does not influence the measured value of the absorption coefficient and propagation velocity of ultrasounds. Apart from this it was found that for liquids with the absorption coefficient $\dfrac{\alpha}{f^2}$ less than 100×10^{-17} s^2/m, and such that the dispersion regions do not occur within the investigated frequency range, the acoustical parameters α and c are the same (within the experimental error) for well purified compunds as for ones only distilled and not submitted to any purification processes. Values, α and c, for these compounds, do not depend on the company they were produced by (Fluka, Schuchard, Koch. Light Laboratory, Reachim or Loba) or on the degree of purity, i.e. whether the compound was pure, analytically pure or pure special for spectroscopy. However, in compounds with higher attenuation small impurities play a significant role, which increases with the increase of the coefficient of ultrasound absorption.

Yet, all investigated liquids were dried and distilled at least once in order to eliminate possible larger solid impurities, water and compounds formed in photoreactions (with time nearly all investigated liquids become brown).

Table 1. Methyl alcohol C_2H_5OH

f MHz	10	17.75	30	45	59.5	410	500	600	850	1000	1100	1250
$\dfrac{\alpha}{f^2}\ \dfrac{s^2}{m}\ 10^{-15}$	34.0	35.1	33.5	34.2	34.1	34.2	34.9	34.7	33.7	33.1	33.9	34.1

Before research was initiated the apparatus was calibrated and checked by performing control measurements for methyl alcohol. Calibration results are presented in Table 1. The α/f^2 values are constant in the investigated frequency range. This is in compliance with data stated by other authors.

All measurements were arried out at a temperature of 293 K in order to eliminate systematic errors of the apparatus.

Classic absorption coefficients were calculated additionally, because they are necessary to determine the α_{exp}/α_{cl} ratio. This ratio indicates whether acoustic dispersion will take place and which processes condition it, and so: if $\alpha_{exp}/\alpha_{cl} > 1$, then acoustical relaxation must occur (only it is of unknown origin and further detailed information about the liquid is necessary to determine what physical phenomenon is responsible for the relaxation process — in our case Kneser interactions); if $\alpha_{exp}/\alpha_{cl} = 1$, then dispersion can occur and it will be caused by shear viscosity relaxation; if $\alpha_{exp}/\alpha_{cl} < 1$, then we are in the dispersion region and viscosity relaxation, η_s, is responsible for the process.

Results and their analysis

Group I

Table 2 presents measurement results for a series of benzene and naphthalen derivatives, namely: amplitude absorption coefficient, classic absorption coefficient calculated from formula (3), density, viscosity, propagation velocity of ultrasounds and α_{exp}/α_{cl} ratio. All liquids from this group, except benzene and toluene (methylbenzene) do not exhibit dispersion regions in the measured frequency range, but values of the classic absorption coefficient $(\alpha_{cl} < \alpha_{exp})$

Table 2

Compound	$\left(\frac{\alpha}{f^2}\right)_{cl}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\varrho\left[\frac{kg}{m^3}\cdot 10^3\right]$	η_s [mPa·s]	$c\left[\frac{m}{s}\right]$	$\frac{\alpha_{exp}}{\alpha_{cl}}$	$\left(\frac{\alpha}{f^2}\right)_{exp}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
p-xylene $C_6H_4(CH_3)_2$	8.6	0.8655 53	0.648 78	1320.1	7.0	59.9
o-xylene $C_6H_4(CH_3)_2$	9.5	0.8845 53	0.804 78	1361.7	6.5	61.7
m-xylene $C_6H_4(CH_3)_2$	7.7	0.8685 53	0.615 78	1340.0	9.9	76.2
pseudocumene $C_6H_3(CH_3)_3$	11.85	0.8748 55	1.01 80	1368.9	4.1	48.1
hemihexamethylbenzene $C_6H_3(CH_3)_3$	11.25	0.8944	1.062	1405.7	4.8	54.1
mesitylene $C_6H_3(CH_3)_3$	8.97	0.8651 55	0.735 80	1355.7	7.27	65.1
isodurene $C_6H_2(CH_3)_4$	—	0.8906 58	—	1410.8	—	60.2

indicate that acoustic relaxation occurs and should be observed at higher frequencies. Measurements were conducted in a range from 1 MHz to 1.3 GHz. When acoustical relaxation processes take place, then observed dispersion regions usually cover two frequency decades (Fig. 2) and thus the acoustic relaxation time, τ_{ak}, can be estimated. (These quantities have been marked τ_{ak} to indicate that relaxation times were determined from acoustical investigations, solely).

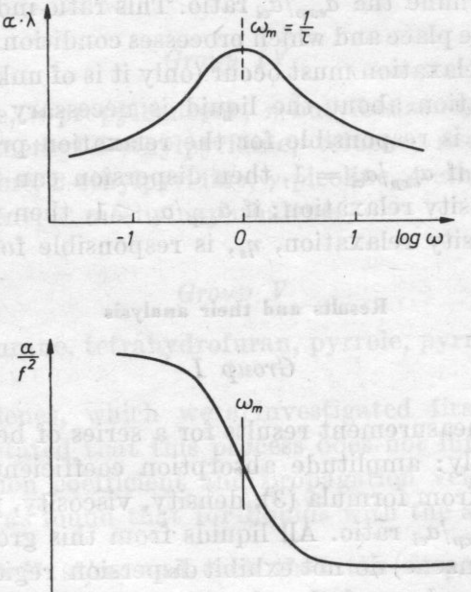


Fig. 2. Dependence between ultrasound absorption (α/f^2 and μ) and the logarithm of the acoustic wave frequency in a dispersive environment (relaxation) with a single relaxation time τ

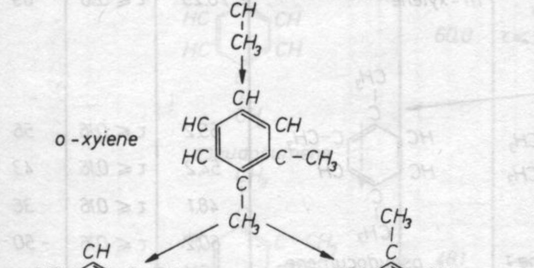
The closest dispersion region can lay above 1.3 GHz and then the inflexion point of the α/f^2 (f^2) curve will be at about 10 GHz, so $\tau_{ak} \leqslant 1.6 \times 10^{-11}$ s. Only the Kneser type relaxation can be expected in the frequency region investigated by the authors in these liquids. If this conclusion is valid, then the performed relaxation time τ should be concurrent with τ_{ak}. Relaxation times, τ, have been calculated from equation (2), making use of the frequency values of free vibrations of the molecule, ν_i, obtained from investigations in the infrared [24–29]. Calculated τ values are of the same order as τ_{ak}, estimated from acoustical measurements (Table 3). This confirms the hypothesis that the relaxation process can be caused by Kneser effects.

Performed investigations indicate that an increase of the number of methyl groups attached to the benzene ring causes a shortening of the relaxation time, so an addition of a group promotes the deactivation of the vibrational degrees

Table 3

Substance	C_p $\left[\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right]$	C_v $\left[\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right]$	C_i $\left[\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right]$	$\left(\frac{a}{f^2}\right)_{exp} - \left(\frac{a}{f^2}\right)_{cl} = A$ $\left[\frac{\mathrm{s}^2}{\mathrm{m}} \cdot 10^{-15}\right]$	τ $\mathrm{s} \cdot 10^{-11}$	τ_{ak} $\mathrm{s} \cdot 10^{-11}$
Benzene 10	134.7	92.9	52.7	841.5	–	28.0
Toluene 31	155.2	113.4	71.1	75.2	–	5.0
o-xylene	188.7 57	147.3	98.3	52.3	1.2	1.6
m-xylene	183.3 57	141.0	92.0	68.5	1.5	1.6
p-xylene	183.7 57	141.0	91.6	51.4	1.1	1.6
mesitylene	207.9 55	163.2	125.1	56.2	0.9	1.6
hemihexamethylbenzene	215.5 55	172.4	132.2	43.0	0.8	1.6
pseudocumene	213.8 55	167.8	130.5	36.3	0.6	1.6
sodurene	241.0 57	199.6	157.7	–	–	–

Table 4. Absorption coefficients and estimated acoustical Kneser relaxation times for methyl derivatives of benzene



$\frac{\alpha}{f^2}\left[\frac{s^2}{m} \cdot 10^{-15}\right]$	$\tau\ [s \cdot 10^{-10}]$	$A\left[\frac{s^2}{m} \cdot 10^{-15}\right]$
860.0	2.8	841
82.0	0.5	75
61.5	$\tau \leqslant 0.16$	52
54.2	$\tau \leqslant 0.16$	43
48.1	$\tau \leqslant 0.16$	36

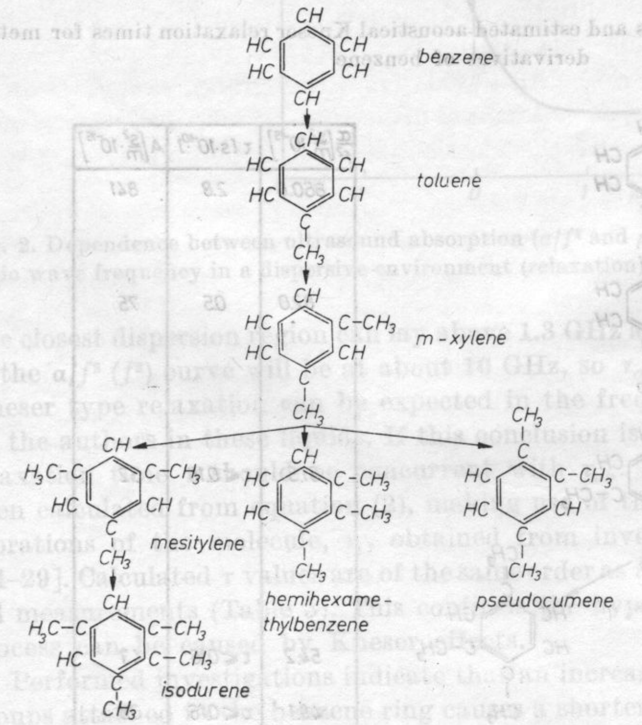
of freedom. (It has to be mentioned that this does not concern arbitrary compounds differing in the number of attached methyl groups, but those that are formed in a series from one another by adding a succeeding group (Tables 4–6) according to the KÖRNER principle).

It has been also found (as it can be seen in the tables) that with the addition of a succeeding methyl group the value of the amplitude absorption coefficient decreases. The addition of the first group causes a very big decrease of the value, while succeeding additions cause smaller drops (Figs. 3–5). The decrease of the absorption coefficient observed in experiments is in accordance with the Herzfeld formula (2):

$$\left(\frac{\alpha}{f^2}\right)_{rel} = A = \frac{2\pi^2\tau}{c}\cdot\frac{C_i(C_p - C_v)}{C_p\cdot C_v}$$

because the addition of a CH_3 group increases the quantity of oscillatory degrees of freedom, thus the thermal capacity, C_i, and thermal capacities, C_p and C_v,

Table 5. Absorption coefficients and estimated acoustical Kneser relaxation times for methyl derivatives of benzene



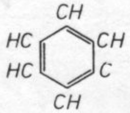
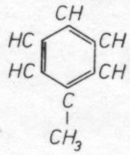
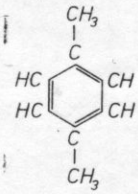
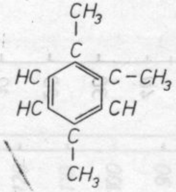
$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot10^{-15}\right]$	$\tau\,[s\cdot10^{-10}]$	$A\left[\frac{s^2}{m}\cdot10^{-15}\right]$
860.0	2.8	841
82	0.16	75
76.25	$\tau \leqslant 0.16$	69
65.2	$\tau \leqslant 0.16$	56
54.2	$\tau \leqslant 0.16$	43
48.1	$\tau \leqslant 0.16$	36
60.2	$\tau \leqslant 0.16$	~ 50

also increase, while the difference $C_p - C_v$ is a nearly constant quantity, so the second factor in the above equation decreases. The relaxation time τ, is shortened and the absorption coefficient has to decrease.

From the point of view of structure this can be explained as follows: the CH_3 group in the ring is a steric hinderence which undergoes a transformation in a collision of heavy and rigid rings with mobile electrons π, which transfer a large amount of energy. The energy transfer is significantly smaller during the collision of light and mobile CH_3 groups. Therefore, an increase of the number of groups decreases the probability of a collision of rings and the energy transfer from the ultrasonic wave to the internal degrees of freedom, what leads to the decrease of the absorption coefficient.

It can be noticed that the addition of succeeding methyl groups causes a decrease of the a_{exp}/a_{cl} ratio (Table 7), so the shear viscosity fraction in the attenuational effect increases.

Table 6. Absorption coefficients and estimated acoustical Kneser relaxation times for methyl derivatives of benzene

	$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\tau\ [s\cdot 10^{-10}]$	$A\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
benzene 	860.0	2.8	84.1
toluene 	82.0	0.5	75
p-xylene 	60.0	$\tau \leqslant 0.16$	51
pseudocumene 	48.1	$\tau \leqslant 0.16$	36

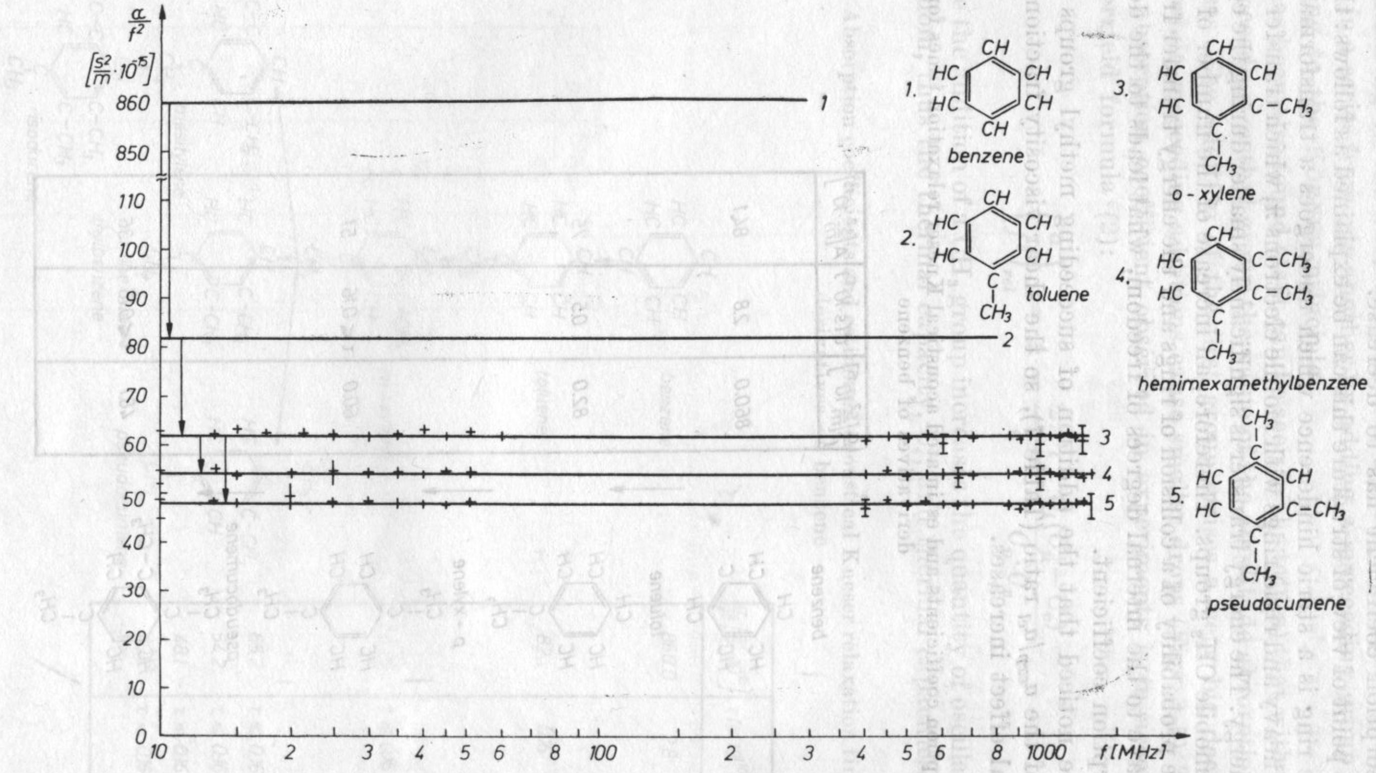


Fig. 3. $a/f^2(f)$ dependence for benzene and benzene methyl derivatives. Arrow ↓ marks the direction of changes of a/f^2 due to an addition of another CH_3 group

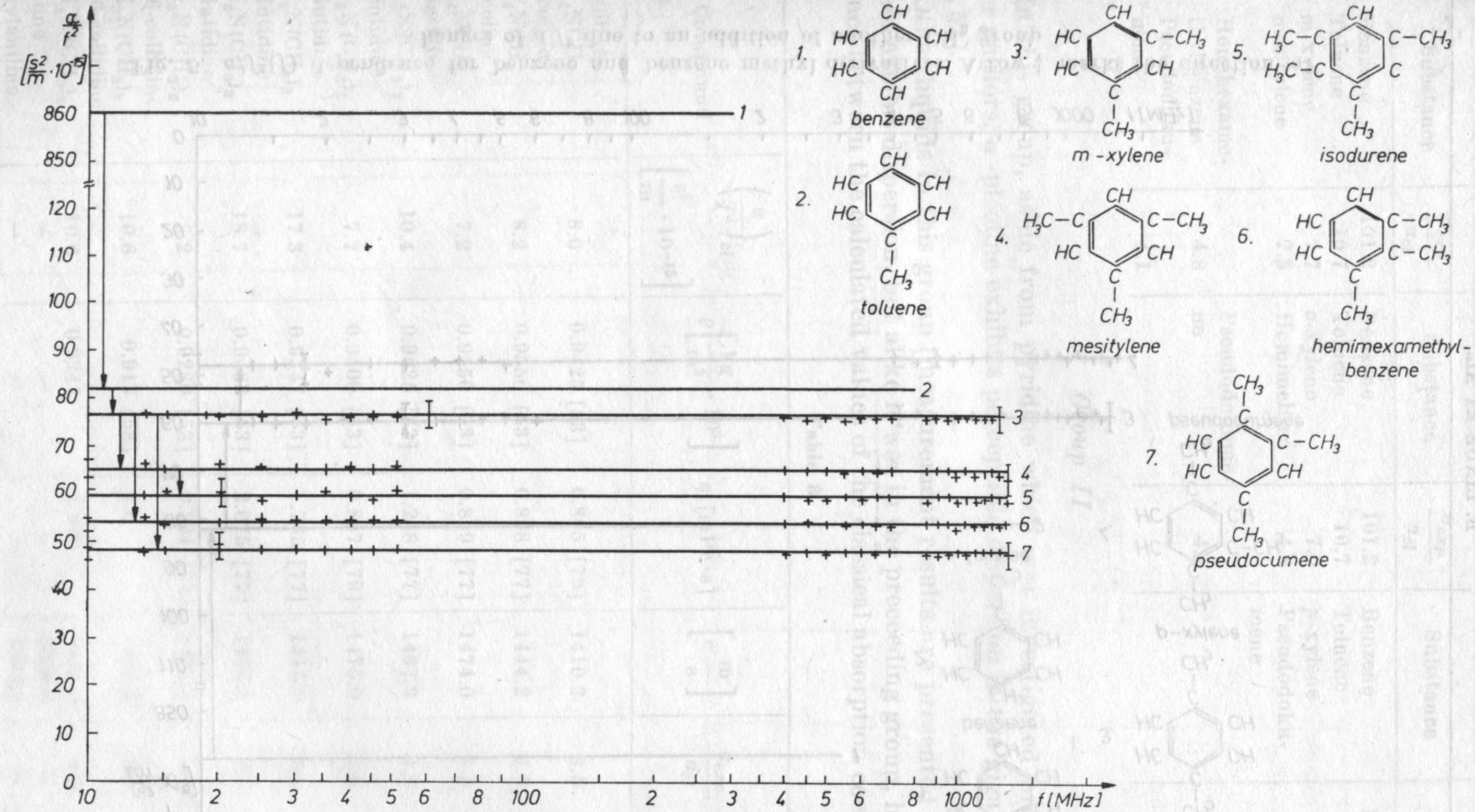


Fig. 4. $\alpha/f^2(f)$ dependence for benzene and benzene methyl derivatives. Arrow ↓ marks the direction of changes of α/f^2 due to an addition of another CH_3 group

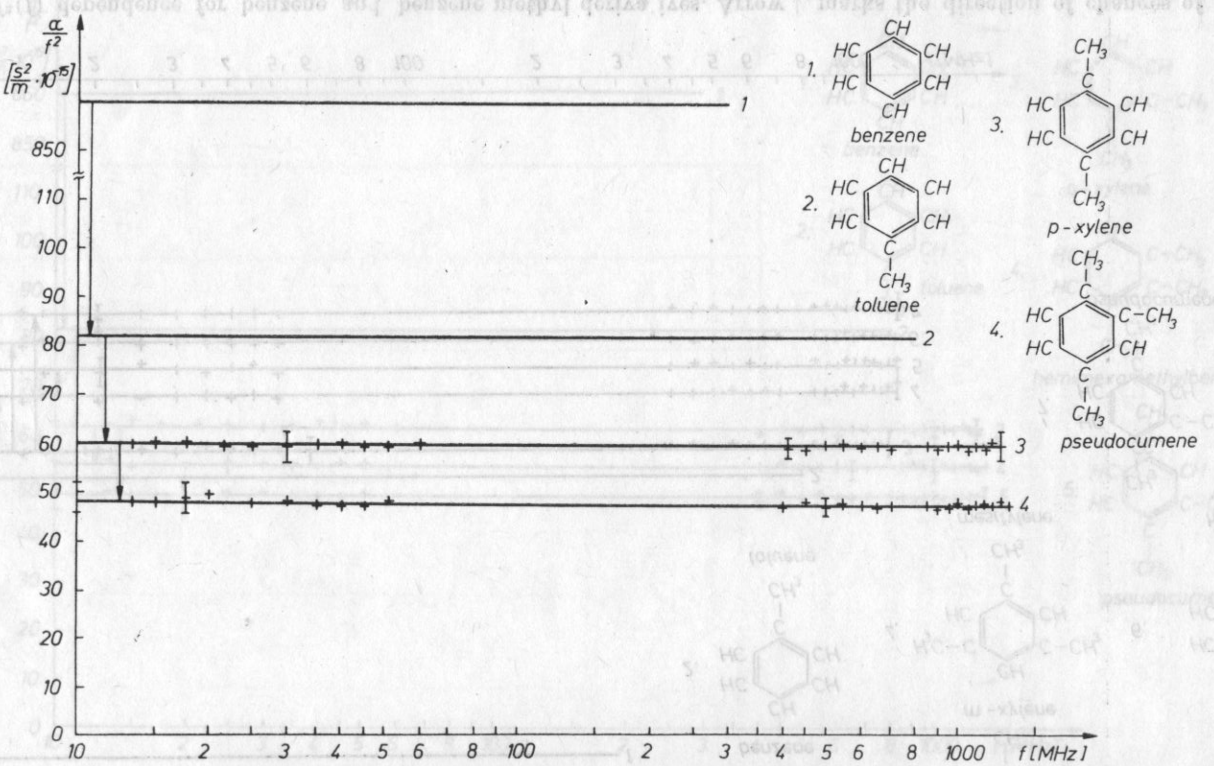


Fig. 5. $\alpha/f^2(f)$ dependence for benzene and benzene methyl derivatives. Arrow ↓ marks the direction of changes of α/f^2 due to an addition of another CH_3 group

Table 7

Substance	$\frac{a_{exp}}{a_{cl}}$	Substance	$\frac{a_{exp}}{a_{cl}}$	Substance	$\frac{a_{exp}}{a_{cl}}$
Benzene	101.2	Benzene	101.2	Benzene	101.2
Toluene	10.7	Toluene	10.7	Toluene	10.7
m-xylene	7.7	*o*-xylene	7.0	*p*-xylene	6.5
mesitylene	7.3	Hemimeliten	4.8	Pseudodokumene	4.1
Hemihexamethylbenzene	4.8	Pseudodokumene	4.1		
Pseudodokumene	4.1				

Group II

In this group, aside from pyridine which was investigated previously by other authors, α -picoline exhibits perceptible dispersion in the gigahertz range [30, 52].

Other liquids in this group (measurement results are presented in Table 8) do not exhibit dispersion, but alike it was in the preceeding group, here the difference between the calculated values of the classical absorption coefficient and

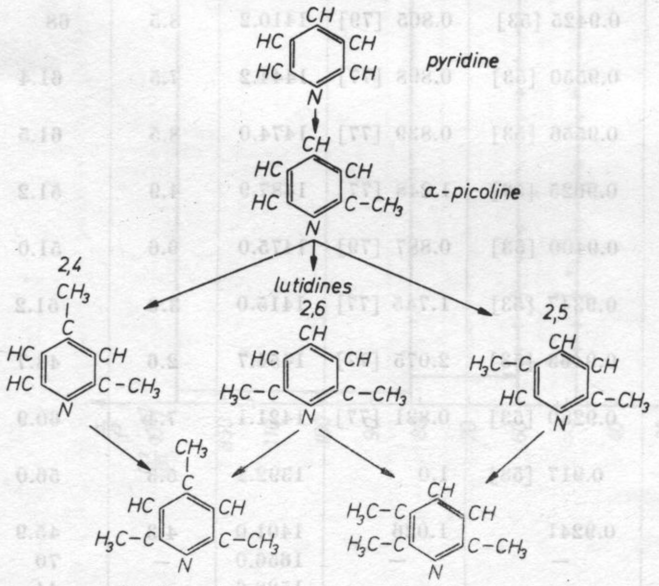
Table 8

Compound	$\left(\frac{\alpha}{f^2}\right)_{cl}$ $\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\varrho\left[\frac{kg}{m^3}\cdot 10^3\right]$	η_s[mPa·s]	$\left[c\ \frac{m}{s}\right]$	$\frac{a_{exp}}{a_{cl}}$	$\left(\frac{\alpha}{f^2}\right)_{exp}$ $\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
α-picoline $C_5H_4NCH_3$	8.0	0.9425 [53]	0.805 [79]	1410.2	8.5	68
β-picoline $C_5H_4NCH_3$	8.2	0.9550 [53]	0.898 [77]	1444.2	7.5	61.4
γ-picoline $C_5H_4NCH_3$	7.2	0.9556 [53]	0.839 [77]	1474.0	8.5	61.5
3,4-lutidine $C_5H_3N(CH_3)_2$	10.4	0.9625 [53]	1.248 [77]	1487.9	4.9	51.2
2,4-lutidine $C_5H_3N(CH_3)_2$	7.7	0.9400 [53]	0.887 [79]	1475.0	6.6	51.0
2,5-lutidine $C_5H_3N(CH_3)_2$	17.3	0.9347 [53]	1.745 [77]	1415.0	3.0	51.2
3,5-lutidine $C_5H_3N(CH_3)_2$	18.7	0.9463 [53]	2.075 [77]	1454.7	2.6	48.7
2,6-lutidine $C_5H_3N(CH_3)_2$	8.2	0.9280 [53]	0.831 [77]	1421.1	7.4	60.9
2,4,6-collidine $C_5H_2N(CH_3)_3$	10.6	0.917 [58]	1.0	1392.2	5.3	56.0
2,3,6-collidine $C_5H_2N(CH_3)_3$	10.6	0.9241	1.026	1401.0	4.3	45.9
Aniline	—	—	—	1656.0	—	70
Ethylaniline	—	—	—	1528.6	—	44

Table 9

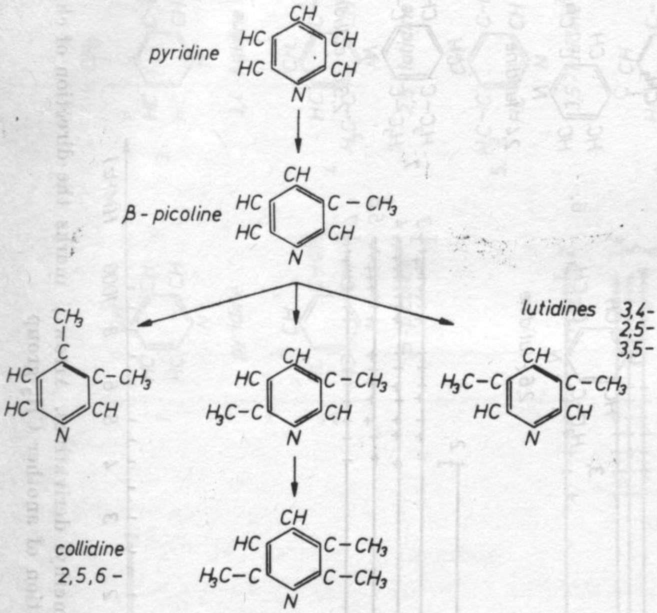
Substance	C_i $\left[\frac{J}{mol \cdot K}\right]$	$A = \left(\frac{\alpha}{f^2}\right)_{exp} - \left(\frac{\alpha}{f^2}\right)_{cl}$ $\left[\frac{s^2}{m} \cdot 10^{-15}\right]$	τ $[s \cdot 10^{-11}]$	τ_{ak} $[s \cdot 10^{-11}]$
Pyridine [10]	46.4	400.0	—	21.0
α-picoline	52.7	60.0	1.5	6.1
β-picoline	49.4	53.3	1.4	1.6
γ-picoline	44.8	54.0	1.6	1.6
2,4-lutidine	74.9	43.1	1.0	1.6
2,5-lutidine	59.4	34.6	0.8	1.6
2,6-lutidine	56.1	52.5	1.3	1.6
3,4-lutidine	68.6	40.6	1.0	1.6
3,5-lutidine	67.8	29.9	0.7	1.6
2,4,6-collidine	83.7	44.6	0.7	1.6
2,5,6-collidine	83.3	35.0	0.9	1.6

Table 10. Absorption coefficients and estimated acoustical Kneser relaxation times for methyl derivatives of pyridine



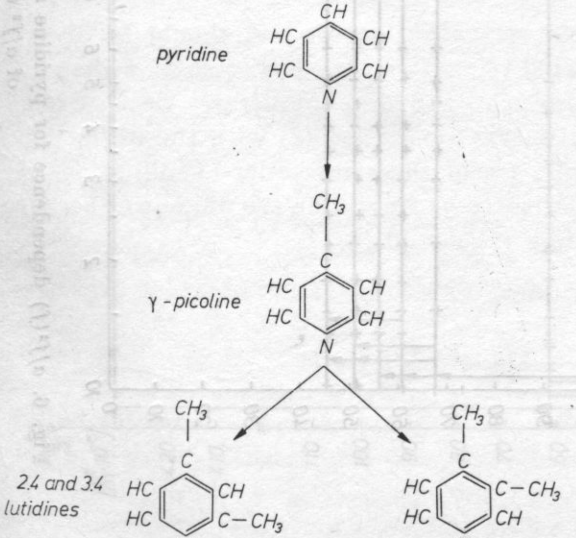
$\frac{\alpha}{f^2}\left[\frac{s^2}{m} \cdot 10^{-15}\right]$	$\tau\,[s \cdot 10^{-10}]$	$A\left[\frac{s^2}{m} \cdot 10^{-15}\right]$
431	2.1	400
68.0	0.16	60
50.8	0.16	43
60.7	0.16	62
51.9	0.16	35
56.2	0.16	46
45.8	0.16	35

Table 11. Absorption coefficients and estimated acoustical Kneser relaxation times for methyl derivatives of pyridine



	$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\tau\,[s\cdot 10^{-10}]$	$A\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
pyridine	431	2.1	400
β-picoline	61.4	$\tau \leqslant 0.16$	53
lutidines 3,4-	51.2	$\tau \leqslant 0.16$	41
2,5-	51.9	$\tau \leqslant 0.16$	35
3,5-	48.8	$\tau \leqslant 0.16$	30
collidine 2,5,6 -	45.8	$\tau \leqslant 0.16$	35

Table 12. Absorption coefficie nts and estimated acoustical Kneser relaxation times for methyl derivatives of pyridine



	$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\tau\,[s\cdot 10^{-10}]$	$A\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
pyridine	431	2.1	400
γ-picoline	61.5	$\tau \leqslant 0.16$	54
2.4 and 3.4 lutidines	50.8	$\tau \leqslant 0.16$	43
	51.2	$\tau \leqslant 0.16$	41

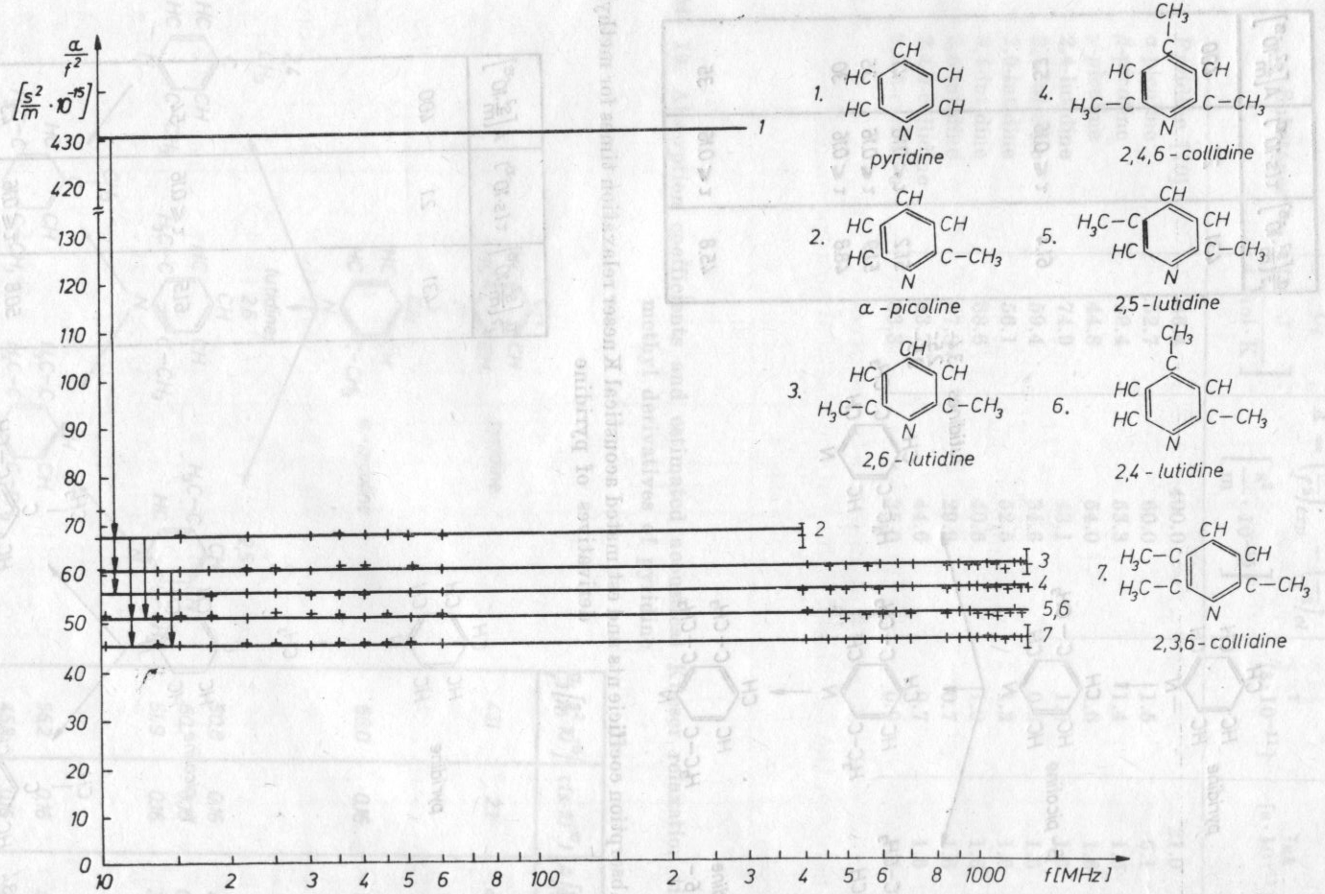


Fig. 6. $\alpha/f^2(f)$ dependence for pyridine and pyridine methyl derivatives. Arrow ↓ marks the direction of changes of α/f^2 due to an addition of another CH_3 group

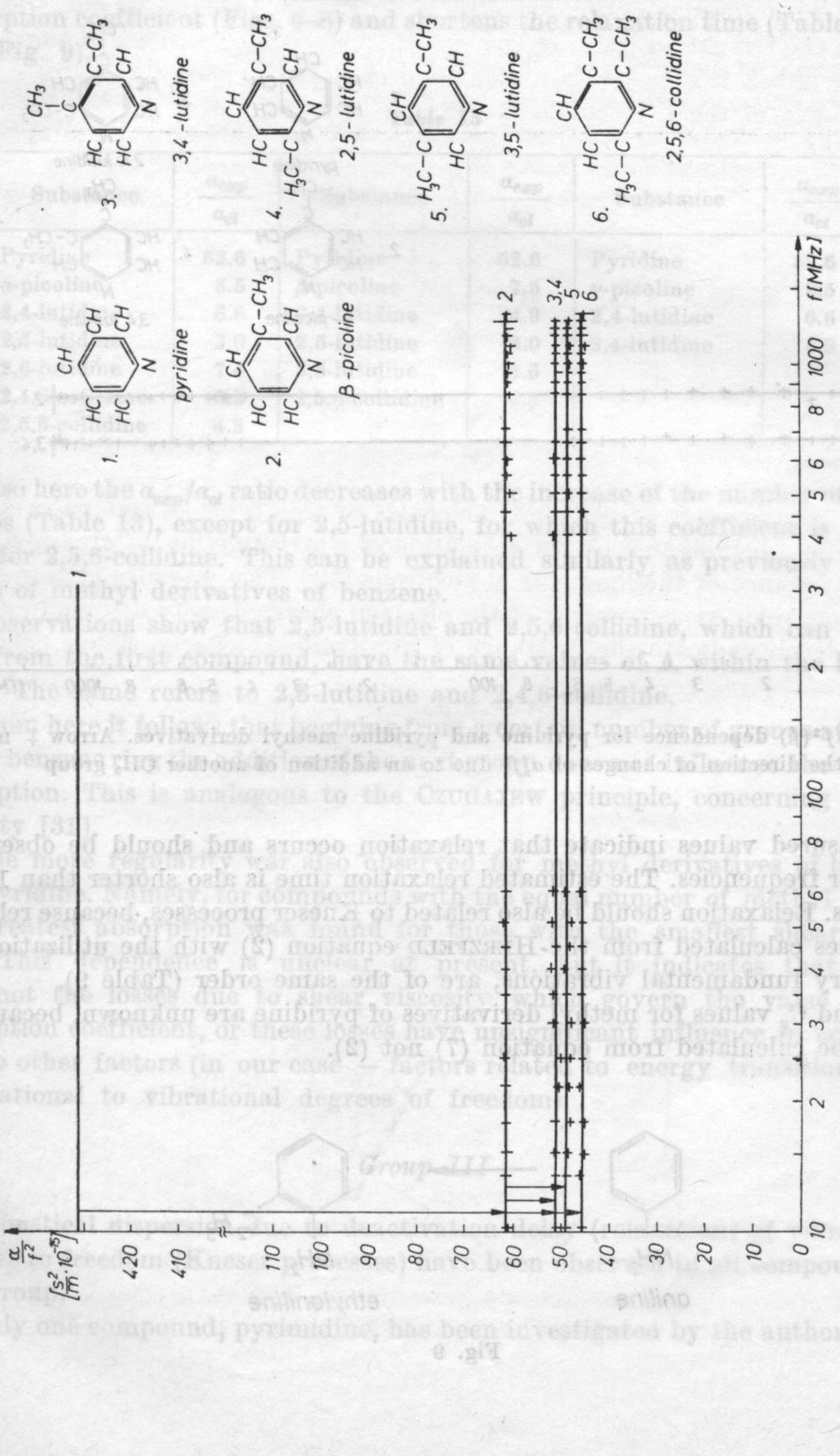


Fig. 7. $\alpha/f^2(f)$ dependence for pyridine and pyridine methyl derivatives. Arrow ↓ marks the direction of changes of α/f^2 due to an addition of another CH_3 group

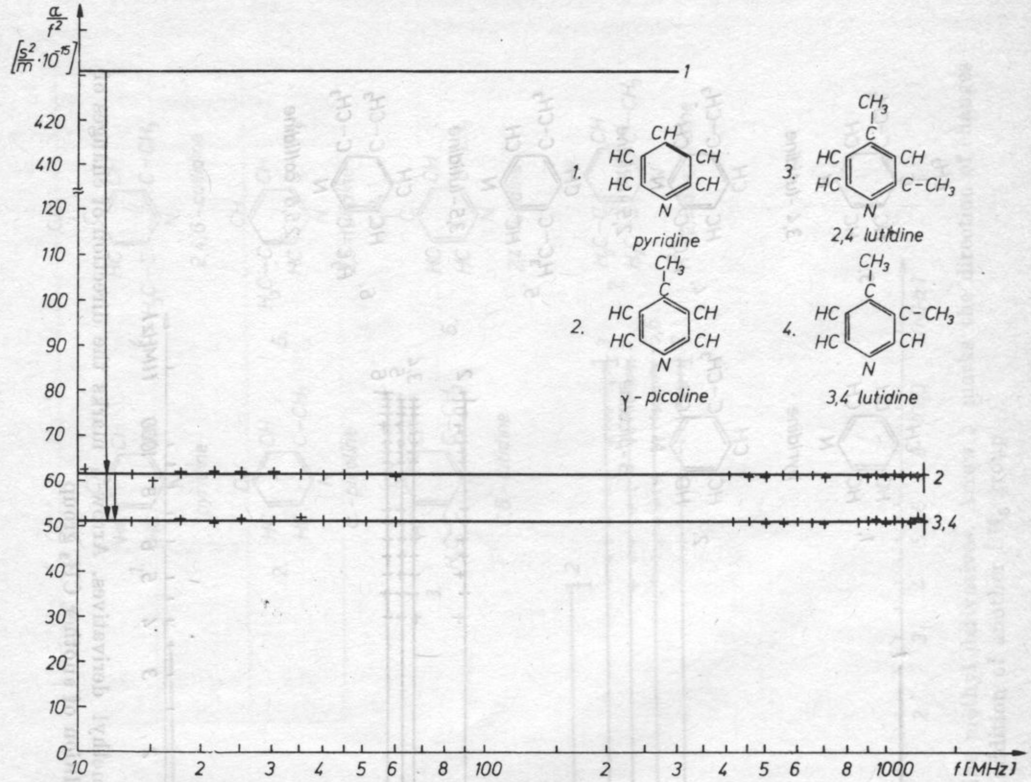


Fig. 8. $\alpha/f^2(f)$ dependence for pyridine and pyridine methyl derivatives. Arrow ↓ marks the direction of changes of α/f^2 due to an addition of another CH_3 group

the measured values indicate that relaxation occurs and should be observed at higher frequencies. The estimated relaxation time is also shorter than $1.6 \times \times 10^{-11}$ s. Relaxation should be also related to Kneser processes, because relaxation times calculated from the HERZFELD equation (2) with the utilization of oscillatory fundamental vibrations, are of the same order (Table 9).

C_p and C_v values for methyl derivatives of pyridine are unknown, because τ had to be calculated from equation (7) not (2).

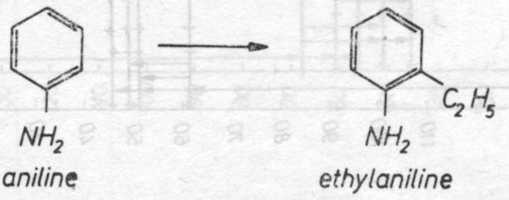


Fig. 9

Liquids belonging to this group exhibit similar dependences between acoustical quantities and the structure as liquids from the first group, namely: the addition of a methyl group causes a decrease of the value of the amplitude absorption coefficient (Figs. 6–8) and shortens the relaxation time (Tables 10–12 and Fig. 9).

Table 13

Substance	$\frac{\alpha_{exp}}{\alpha_{cl}}$	Substance	$\frac{\alpha_{exp}}{\alpha_{cl}}$	Substance	$\frac{\alpha_{exp}}{\alpha_{cl}}$
Pyridine	52.6	Pyridine	52.6	Pyridine	52.6
α-picoline	8.5	β-picoline	7.5	γ-picoline	8.5
2,4-lutidine	6.6	3,4-lutidine	4.9	2,4-lutidine	6.6
2,5-lutidine	3.0	2,5-lutidine	3.0	3,4-lutidine	4.9
2,6-lutidine	7.4	3,5-lutidine	2.6		
2,4,6-collidine	5.3	2,5,6-collidine	4.3		
2,5,6-collidine	4.3				

Also here the α_{exp}/α_{cl} ratio decreases with the increase of the number of methy groups (Table 13), except for 2,5-lutidine, for which this coefficient is smaller than for 2,5,6-collidine. This can be explained similarly as previously for the group of methyl derivatives of benzene.

Observations show that 2,5-lutidine and 2,5,6-collidine, which can be formed from the first compound, have the same values of A within the limit of error. The same refers to 2,3-lutidine and 2,4,6-collidine.

From here it follows that begining from a certain number of groups attached to the benzene ring the addition of the next group does not influence the $(\alpha/f^2)_{rel}$ absorption. This is analogous to the CZUGAJEW principle, concerning optical activity [31].

One more regularity war also observed for methyl derivatives of benzene and pyridine. Namely, for compounds with the equal number of methyl groups the greatest absorption was found for those with the smallest shear viscosity. This dependence is unclear at present, but it indicates that either it is not the losses due to shear viscosity which govern the value of the absorption coefficient, or these losses have unsignificant influence in comparison to other factors (in our case – factors related to energy transition from translational to vibrational degrees of freedom).

Group III

Acoustical dispersion due to deactivation delay (relaxation) of vibrational degrees to freedom (Kneser processes) have been observed in all compounds in this group.

Only one compound, pyrimidine, has been investigated by the authors [30].

The comparison of compounds in this group leads to the following conclusions: an interchange of a carbon to a nitrogen decreases absorption and shortens the relaxation time. This may seem contradictory to what was said previously, that a steric hindrance in the ring, such as a CH_3 group, decreases damping and shortens the relaxation time; so the detachment of one hydrogen should cause a reverse effect. It appears that a lone pair of electrons from the nitrogen atom replaces one of the C-H bonds in benzene (Fig. 10).

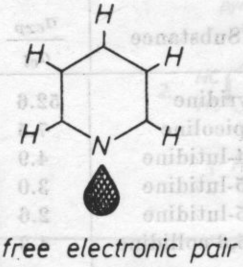


Fig. 10. Pyridine with a cloud from the lone pair of electrons from nitrogen

The fundamental property of molecules of this type — this pairs proton receptivity accompanied by the formation of a pyridine ion — gives evidence of the existance of the lone pair of electrons [32]. This was also confirmed by rentgenographic measurements of the electron charge density distribution [33], which clearly indicate the existance of "protruding" charge clouds (Fig. 11).

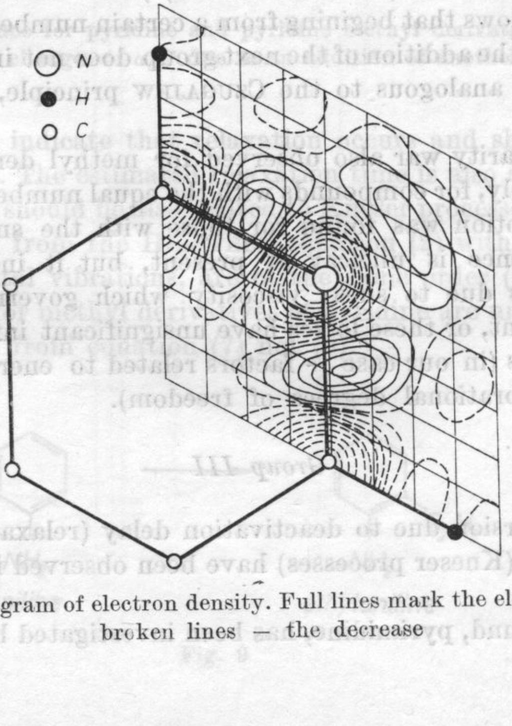


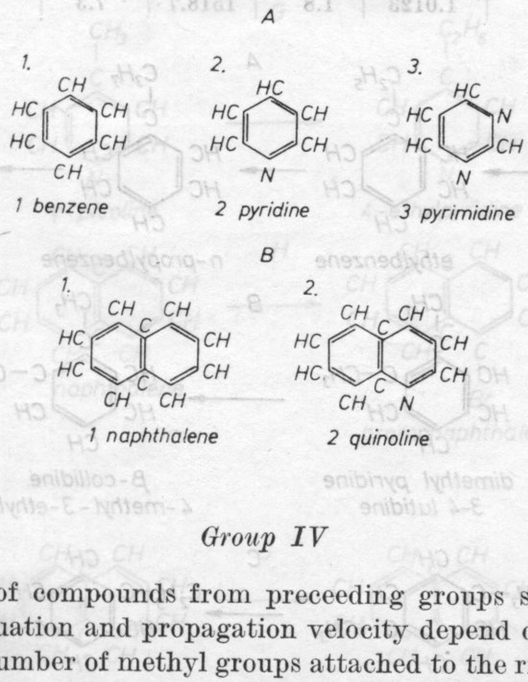
Fig. 11 Differential diagram of electron density. Full lines mark the electron density increase, broken lines — the decrease

Such a steric hindrance is far smaller than the larger CH_3 group, so changes in absorption and the relaxation time should be smaller. This conclusion is confirmed by acoustical data obtained for the entire group of compounds (Table 14.) From benzene to toluene (group I) absorption decreases about ten times and, the relaxation time about six times, while in a series from benzene to pyridine the analogical quantities decrease two and less than two times, respectively.

The ratios of absorption and the relaxation time for naphthalene and quinoline are even smaller, because the influence of the cloud, which results from two lone electrons, is probably negligible in such large compounds.

Table 14

substance	$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\tau_{ak}\,[s\cdot 10^{-11}]$	references
A1	860	2.8	21, 34, 35, 36, 37
A2	431	2.1	23, 34, 37, 38
A3	120	1.2	
B1	275	0.6	39
B2	163	0.3	14



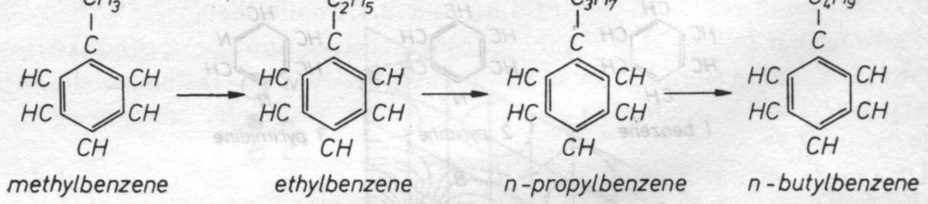
Group IV

Investigations of compounds from preceeding groups showed that values of acoustical attenuation and propagation velocity depend on the steric hindrance, i.e. on the number of methyl groups attached to the ring and on whether a methyl group or an electron cloud formed the hindrance. This indicated that the enlargement of a group attached to the ring should give similar effects.

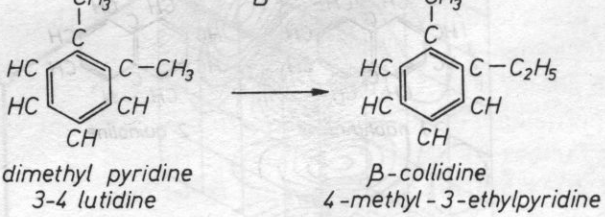
Table 15

Compound	$\left(\frac{\alpha}{f^2}\right)_{cl}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\varrho\left[\frac{kg}{m^3}\cdot 10^3\right]$	η_s[mP·s]	$c\left[\frac{m}{s}\right]$	$\frac{\alpha_{exp}}{\alpha_{cl}}$	$\left(\frac{\alpha}{f^2}\right)_{exp}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	References
A1						82	[40, 41] [42, 43]
A2						55	[44, 45]
A3						56	[45,50]
A4						55	[45]
B1	10.4	0.9625	1.248	1487.9	4.9	51.2	
B2		0.9	—	1486.1	—	42.3	
C1	17.3	0.9347	1.745	1415.0	3.0	51.2	
C2				1388.0		50.6	
D1					10.7	82.0	
D2				1593.4		40.5	
E1	8.0	0.9425	0.805	1410	8.5	68	
E2				1383.6		46.1	
F1					10.7	82	
F2				1486.2		31	
G1	7.2	0.9556	0.839	1474.0	8.5	61.5	
G2	8.6	0.936	0.91	1439.4	4.0	34.2	
H1 and I2						275	
H2	41.8	1.4839	6.2	1380.2	3.4	142.7	
I2	13.4	1.0123	1.8	1518.7	7.3	97.3	

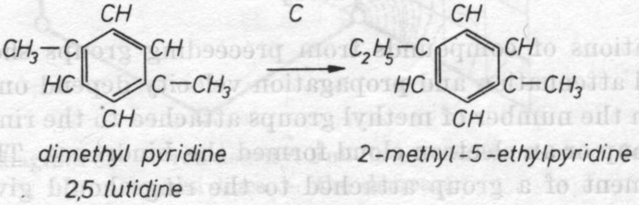
A



B



C



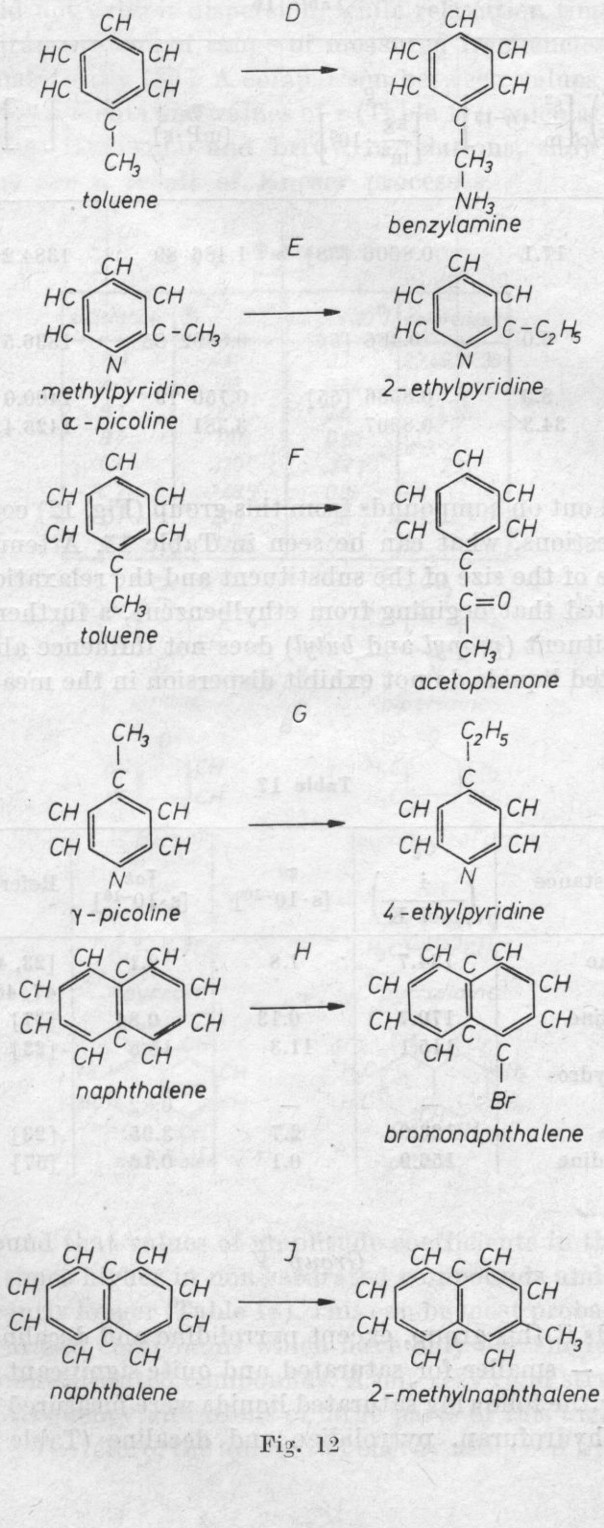

D
toluene
benzylamine
E
methylpyridine
α-picoline
2-ethylpyridine
F
toluene
acetophenone
G
γ-picoline
4-ethylpyridine
H
naphthalene
bromonaphthalene
J
naphthalene
2-methylnaphthalene

Fig. 12

Table 16

Compound	$\left(\frac{\alpha}{f^2}\right)_{cl}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	ϱ $\left[\frac{kg}{m^3}\cdot 10^3\right]$	η_s [mP·s]	$c\left[\frac{m}{s}\right]$	$\frac{\alpha_{exp}}{\alpha_{cl}}$	$\left(\frac{\alpha}{f^2}\right)_{exp}$ $\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
Piperidine $C_5H_{11}N$	17.1	0.8606 [58]	1.486 89	1384.2	5.0	78.4
Tetrahydrofuran C_4H_8O	6.0	0.486 [56]	0.8892 85	1336.5	18.3	99.1
Pyrrolidine C_4H_9N	8.5	0.8586 [55]	0.756 79	1400.0	5.2	43.5
Decaline	34.3	0.8967	3.381	1425.4	3.5	120.0

Research carried out on compounds from this group (Fig. 12) confirmed mentioned above suggestions, what can be seen in Table 15. Attenuation decreases with the increase of the size of the substituent and the relaxation time is shortened. It was stated that begining from ethylbenzene, a further increase of the size of the substituent (*propyl* and *butyl*) does not influence absorption.

All investigated liquids do not exhibit dispersion in the measured frequency range.

Table 17

Substance	C_i $\left(\frac{i}{mol\cdot K}\right)$	τ $[s\cdot 10^{-10}]$	τ_{ak} $[s\cdot 10^{-10}]$	References
Pyridine	134.7	1.8	2.1	[23, 46, 47, 48]
Piperidine	170.7	0.13	0.84	[57]
Furan	115.1	11.3	15.5	[23]
Tetrahydrofuran	—	—	0.82	
Pyrrole	123.0	2.7	3.95	[23]
Pyrrolidine	156.9	0.1	0.16	[57]

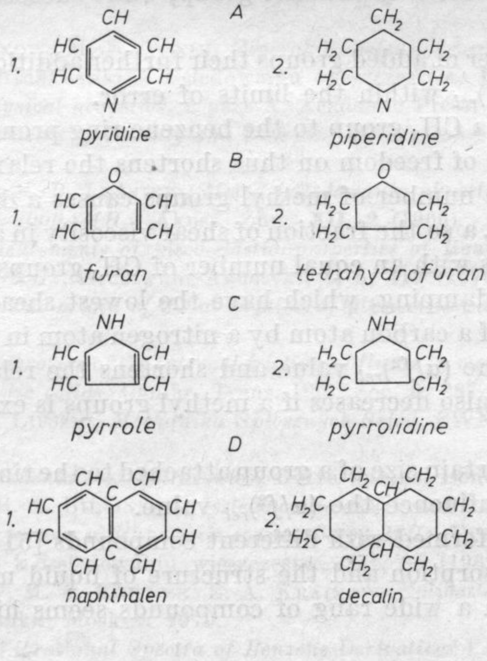
Group V

All compounds it this group, except pyrrolidine and decaline, exhibit acoustical dispersion — smaller for saturated and quite significant for unsaturated compounds. Only the following saturated liquids were measured by the authors: piperidine, tetrahydrofuran, pyrrolidine and decaline (Table 18).

Pyrrolidine did not exhibit dispersion, while relaxation times for piperidine and tetrahydrofuran are out of range of measured frequencies [30]. They can be determined analytically [30]. A comparison between values of τ_{ak} estimated from acoustic measurements and values of τ (Table 17), calculated from formula (6) with simplifying HERZFELD and LITOWITZ relations, shows that observed dispersion regions are a result of Kneser processes.

Table 18

substance	$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\tau_{ak}\,[s\cdot 10^{-10}]$	references
A 1	431	2.1	23,46,37,38
A 2	85	0.84	
B 1	2100	12.6	23,38
B 2	110	0.82	
C 1	370	3.2	23
C 2	43.5	0.16	
D 1	275	0.6	14
D 2	120.5	0.16	



It was also found that values of amplitude coefficients in the low frequency range are many times higher in non-saturated compounds and their relaxation times are significantly longer (Table 18). This can be most probably explained by the fact that saturated compounds which have only one single bond are much more rigid than non-saturated compounds. A not very rigid structure of a molecule permits low frequency vibrations of large parts of this molecule in relation to each other [14]. Therefore, the amount of energy absorbed by such a molecule is smaller and given up to the surroundings more rapidly. This is also valid for compounds in which absorption is influenced by two factors: Kneser effects and rotary isomeric transition [15]. (In transitions from benzene to cyclohexane [23] and from naphthalene to decaline [39, 49], absorption and relaxation time values are significantly lower than in benzene and naphthalene, although in cyclohexane and decaline aside from Kneser absorption also absorption due to *cis-trans* isomeric transition occurs.)

Conclusions

Investigations performed on a series of cyclic compounds have led to the determination of certain dependences between the amplitude absorption coefficient, $(\alpha/f^2)_{rel}$, and the structure of the liquid, namely:

1. The addition of a CH_3 group to a benzene ring causes a decrease of the amplitude absorption coefficient. The value of $(\alpha/f^2)_{rel}$ decreases quite significantly with the addition of the first group, while succeeding additions cause smaller changes.
2. At a certain number of added groups their further addition does not influence the value of $(\alpha/f^2)_{rel}$ within the limits of error.
3. Every addition of a CH_3 group to the benzene ring promotes deactivation of oscillatory degrees of freedom on thus shortens the relaxation time.
4. An increase of the number of methyl groups causes a decrease of the value of the α_{exp}/α_{cl} ratio, a so the fraction of shear viscosity in absorption increases.
5. Among compounds with an equal number of CH_3 groups those are characterized by greatest damping, which have the lowest shear viscosity.
6. The replacement of a carbon atom by a nitrogen atom in a benzene ring causes a decrease of the $(\alpha/f^2)_{rel}$ value and shortens the relaxation time.
7. The $(\alpha/f^2)_{rel}$ value also decreases if a methyl groups is exchanged by a larger one.
8. After reaching a certain size of a group attached to the ring, a further increase of size does not influence the $(\alpha/f^2)_{rel}$ value.

Investigations performed with different compounds [51] also indicate strict relations between absorption and the structure of liquid molecules. Therefore, further research with a wide rang of compounds seems highly advisable.

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