

Structural peculiarities of salts of 2,2,6,6-tetramethyl-4-piperidinol with aliphatic monocarboxylic acids

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Dedicated to Professor RNDr. V. Sutoris, CSc. and Professor Ing. J. Kováč, DrSc., in honour of their 60th birthdays

Salts of 2,2,6,6-tetramethyl-4-piperidinol with aliphatic monocarboxylic acids with 2, 4, 6, 8, 12, 16, and 18 carbons have been prepared. Their structures were established by spectral methods and X-ray structure analysis. It has been found that the salts of aliphatic acids with 2, 4, 6, and 8 carbons form crystalline salts where the amount of substance ratio of components is 1 : 1, while this ratio of components in crystalline salts of aliphatic acids with 12, 16, and 18 carbons is 1 : 2.

Получены соли 2,2,6,6-тетраметил-4-пиперидинола с алифатическими монокарбоновыми кислотами с 2, 4, 6, 8, 12, 16 и 18 углеродными атомами. Их строение было определено с помощью спектроскопических методов и рентгеноструктурного анализа. Обнаружено, что алифатические кислоты с 2, 4, 6 и 8 углеродными атомами образуют кристаллические соли, в которых компоненты находятся в соотношении 1 : 1, в то время как в кристаллических солях алифатических кислот с 12, 16 и 18 углеродными атомами это соотношение равно 1 : 2.

Extensive utilization of the compounds derived from 2,2,6,6-tetramethyl-piperidine as light stabilizers started in 1967 [1]. Since then the interest in these saturated heterocyclic compounds has grown continuously. Beside application in stabilization of polymers [2, 3], these derivatives have been utilized in medicine [4], colour photography [5], stabilization of dispersed dyes [6], and numerous other fields.

2,2,6,6-Tetramethyl-4-piperidinol (TMP) is a significant intermediate in production of many derivatives (Fig. 1). Its two polar groups enable to enter series of reactions and the molecule may occupy different positions in crystal structures.

Andrews [7] used dilithium salt of TMP as catalyst in preparation of methacrylate polymers which showed high stability. The salts of aliphatic acids with TMP have been described as very effective light stabilizers [8].

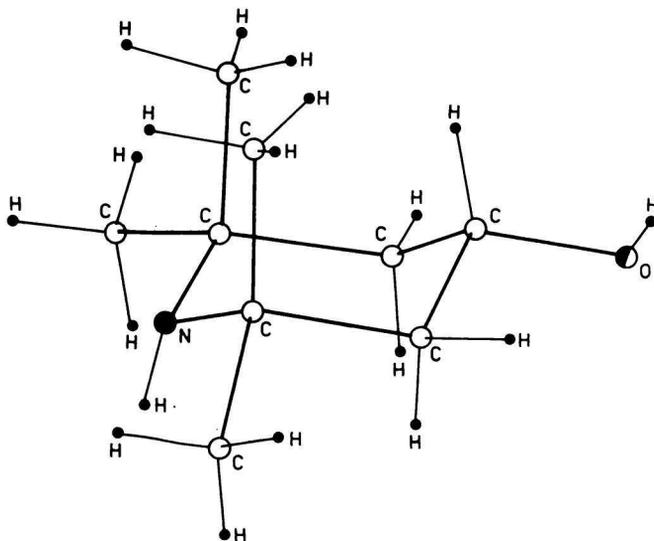
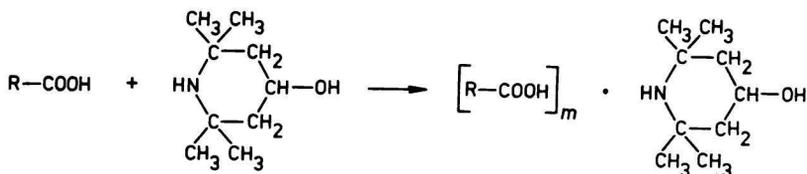


Fig. 1. 2,2,6,6-Tetramethyl-4-piperidinol.

We have dealt with synthesis and structure determination of salts of TMP with aliphatic monocarboxylic acids. It has been found that the prepared salts of TMP with aliphatic monocarboxylic acids with carbons equal to and less than 8 form crystal salts where the components are in the amount of substance ratio $n(\text{TMP}) : n(\text{acid}) = 1 : 1$. The salts of TMP with aliphatic acids with carbons equal to and higher than 12 form salts the components of which are in the ratio $n(\text{TMP}) : n(\text{acid}) = 1 : 2$ (Scheme 1). We have fully confirmed this fact analytically and by measuring the crystal and molecular structures of salts of TMP with hexanoic [9] and dodecanoic [10] acids.



$$\text{R} = \text{CH}_3 - (\text{CH}_2)_n, \quad n = 0, 2, 4, 6, 10, 14, 16$$

$$m = 1 \text{ when } n = 0, 2, 4, 6$$

$$m = 2 \text{ when } n = 10, 14, 16$$

Scheme 1

Experimental

Characterization of the prepared salts is presented in Table I. Melting points were determined on a Kofler stage. The acid values of the prepared salts were determined titrimetrically with 0.1 M-KOH solution using phenolphthalein as the indicator.

Table I

Characterization of the prepared salts

Compound	<i>n</i>	<i>m</i>	Formula	<i>M_r</i>	<i>w_i</i> (calc.)/% <i>w_i</i> (found)/%			M.p./°C	Acid value calc. found
					C	H	N		
					<i>I</i>	0	1		
<i>II</i>	2	1	C ₁₃ H ₂₇ NO ₃	245.4	63.57 64.34	11.00 11.45	5.70 5.92	151—152	244.7 243.8
<i>III</i>	4	1	C ₁₅ H ₃₁ NO ₃	273.5	65.81 65.88	11.33 12.15	5.12 5.30	103—104	205.2 205.8
<i>IV</i>	6	1	C ₁₇ H ₃₅ NO ₃	301.5	67.64 67.74	11.60 12.05	4.64 4.64	95—96	186.1 190.6
<i>V</i>	10	2	C ₃₃ H ₆₇ NO ₅	557.0	70.47 71.10	12.02 12.87	2.51 2.50	66—68	201.2 206.6
<i>VI</i>	14	2	C ₄₁ H ₈₃ NO ₅	669.0	73.51 73.59	12.40 13.18	2.08 2.28	79—80	167.6 169.2
<i>VII</i>	16	2	C ₄₅ H ₉₁ NO ₅	725.0	74.35 74.60	12.54 13.29	1.93 2.04	91—92	154.6 159.4

IR spectra of all salts were measured with a UR 20 (Zeiss, Jena) apparatus in tetrachloromethane. All spectra displayed bands $\nu(\text{NH}_2^+)$ at $\tilde{\nu} = 2500\text{--}2700\text{ cm}^{-1}$ and $\delta(\text{NH}_2^+)$ at $\tilde{\nu} = 1580\text{--}1600\text{ cm}^{-1}$.

¹H NMR spectra of the prepared compounds (5—10% solutions in CDCl₃) were measured with a Tesla BS 487 A spectrometer at working frequency of 60 MHz and room temperature. The ¹H NMR spectra of salts of TMP with dodecanoic, hexadecanoic, and octadecanoic acids were measured with addition of an internal standard (1 equiv. of naphthalene per 1 equiv. of quaternary salt) for more precise reading of integration. The ¹H NMR spectra revealed a wide multiplet at $\delta = 0.7\text{--}2.5$ ppm for all hydrogens except >CH—O—, the multiplet of which appeared at $\delta = 3.8\text{--}4.2$ ppm.

In determination of crystal and molecular structures of salts diffractometric measurements were performed with a Syntex P21 automatic diffractometer. In elucidation of structures direct methods of the Multan 78 program were used. Calculations were performed with an EC 1033 computer by using NRC programs. Precise description of conditions of measurement and evaluations are reported in papers [9, 10].

Salts of 2,2,6,6-tetramethyl-4-piperidinol with aliphatic monocarboxylic acids

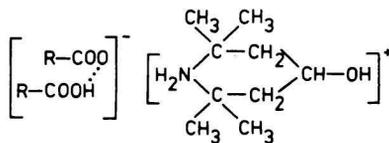
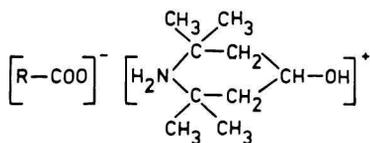
The solution of TMP (1 mol) in diethyl ether (150 cm³) was placed into a 250-cm³ three-necked flask and the respective acid (1 mol), dissolved in diethyl ether (40 cm³), was added dropwise during 20 min at room temperature under continuous stirring. The reaction mixture was agitated for another 60 min. The precipitate was filtered and crystallized several times until constant melting point. Acetone and hexane were used as crystallization solvents.

In the reactions with hexanoic and dodecanoic acids the precipitate was not formed. The reaction mixture was refluxed for 4 h, the solvent was evaporated and the solid was crystallized to constant melting point.

The salt of TMP with octadecanoic acid was prepared in several ways: by reacting the components in the $n(\text{TMP}) : n(\text{acid})$ ratios of 1 : 1, 1 : 2, 2 : 1, and 3 : 1 at 25 °C, 35 °C, and 80 °C in diethyl ether and ethanol. The compounds isolated in all cases were the same with constant melting point.

Discussion

The two polar groups of TMP ($>\text{NH}$ and $-\text{OH}$), able to form hydrogen bondings, play an important role in formation of salts of TMP with aliphatic monocarboxylic acids. The results obtained indicate an essential difference in structures of TMP salts in dependence on the used aliphatic monocarboxylic acid. The salts prepared from TMP and aliphatic monocarboxylic acids with 2 to 8 carbons formed crystals where the ratio $n(\text{TMP})$ to $n(\text{acid})$ was 1 : 1, while in the case of acids with 12 to 18 carbons this ratio was 1 : 2. This fact was first recognized in determination of the acid values of the formed salts and proved by elemental analysis and NMR spectra. According to X-ray structure analysis, TMP with hexanoic and dodecanoic acids forms internal salts of the following type



The ionized form of the given cation has the chair conformation with equatorial orientation of the OH group.

A comparison of melting points of salts with increasing relative molecular mass (*I-VII*) indicates an essential change in their structures. The melting points of the salts prepared from aliphatic monocarboxylic acids with 2, 4, 6, and 8 carbons decrease linearly in spite of the increasing molecular mass, while

those of the salts prepared from acids with 12, 14, and 18 carbons increase moderately with the increasing relative molecular mass (Fig. 2). The decrease of melting points of the salts prepared from acids containing 2 to 8 (to 10?) carbons indicates an increasing tension in the crystal lattice.

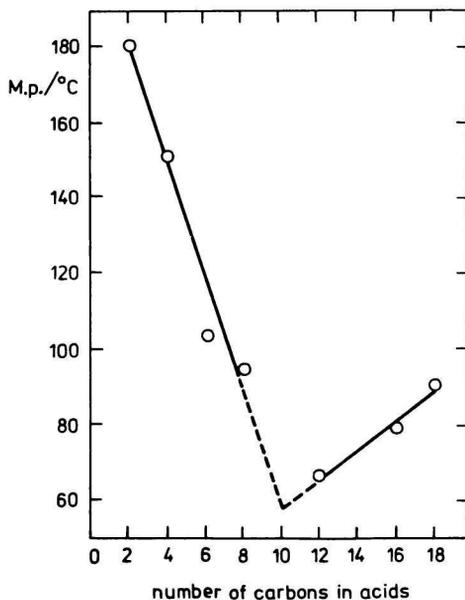


Fig. 2. Melting points of salts of TMP in dependence on the number of carbons in aliphatic acids.

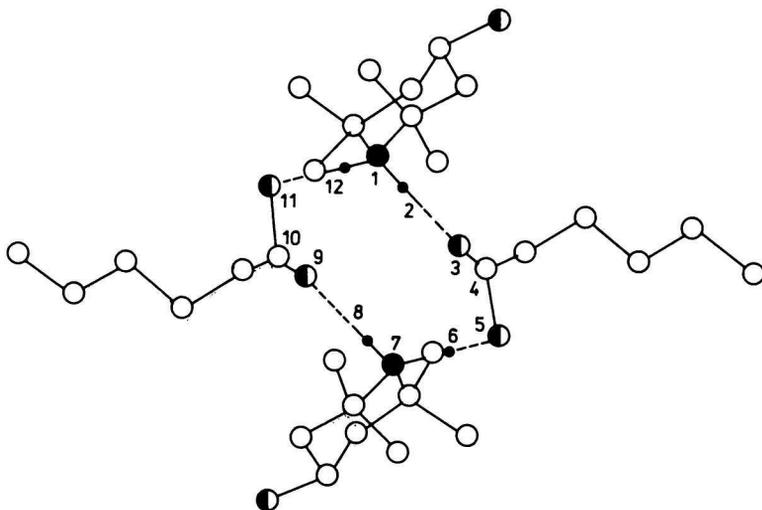


Fig. 3. Basic 12-membered ring of the salt of TMP with hexanoic acid.

● Nitrogen; ○ oxygen; ○ carbon; ● hydrogen.

Only those hydrogens were marked which formed hydrogen bonds and were suitable to control the number of atoms in the rings.

The X-ray structure analysis of the salt of TMP with hexanoic acid shows that the basic 12-membered rings are formed alternately with carboxyl groups of two acids and amino groups of two TMP in the ionized form [9] (Fig. 3). The bond length C=O in carboxyl group is 1.268×10^{-10} m and 1.254×10^{-10} m and the distance between hydrogen atoms and nitrogen is 0.888×10^{-10} m and 1.042×10^{-10} m, respectively.

The basic 12-membered rings are interconnected through hydrogen bonding of OH group of one basic 12-membered ring with oxygen of carboxyl group of the second 12-membered ring. Association of 4 basic 12-membered rings results in large, 36-membered rings which form cavities. The carbon chains of two aliphatic acids are directed into this cavity. By elongation of the aliphatic chain the tension of this cavity increases and in the salt of dodecanoic acid such a lattice cannot be formed due to sterical reasons (Fig. 4).

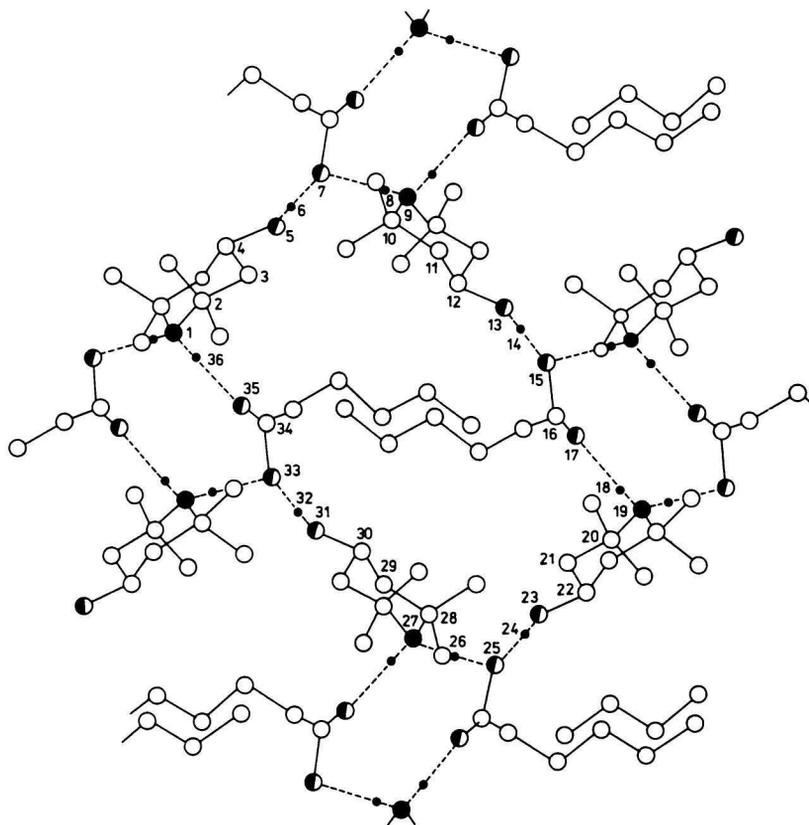


Fig. 4. Projection of the structure of the salt of TMP with hexanoic acid. Denotation is the same as in Fig. 3.

Quite different situation arises in the formation of a crystal salt of TMP with dodecanoic acid. The basic 14-membered rings are formed by carboxyl group of aliphatic acid in ionized form (the measured bond length C=O was 1.325×10^{-10} m and 1.269×10^{-10} m, respectively), OH group of TMP, another TMP molecule which is bound by hydrogen bond of NH group to oxygen of the OH group of the foregoing TMP, and by oxygen of the OH group bound to NH group of the third TMP, involved in formation of basic 14-membered rings. The second aliphatic acid is bound by hydrogen bond of carboxyl group to oxygen of the acid which is included in the 14-membered ring. Another pair of aliphatic acids is bound to oxygen of OH group of TMP, the NH and OH groups of which are included in the basic 14-membered ring. The carboxyl group of this pair of aliphatic acids is part of the subsequent 14-membered ring (Fig. 5). In

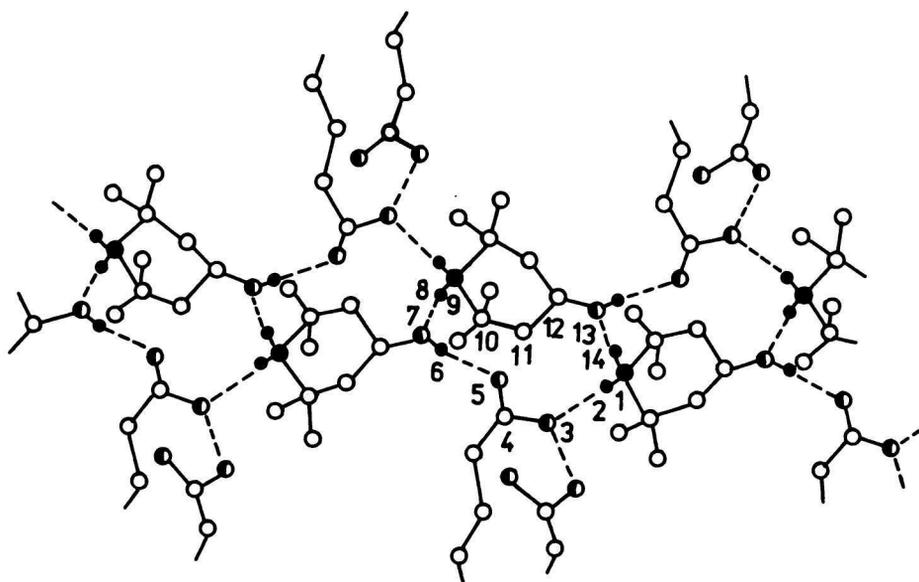


Fig. 5. Basic 14-membered ring of the salt of TMP with dodecanoic acid. Denotation is the same as in Fig. 3.

such a structure the ratio $n(\text{TMP}) : n(\text{aliphatic acid})$ is 1 : 2. In this way associated 14-membered rings form apparently one layer. As follows from X-ray structure analysis, the crystal lattice is formed by antiparallel arrangement of the hydrocarbon chains of aliphatic acids (Fig. 6). The individual layers in the layered structure are formed by 14-membered rings associated by hydrogen bondings. The layers are separated by carbon chains of aliphatic acids, which are held together by van der Waals forces. This structure is very similar to that of the complex of TaS₂ with octadecylamine [11].

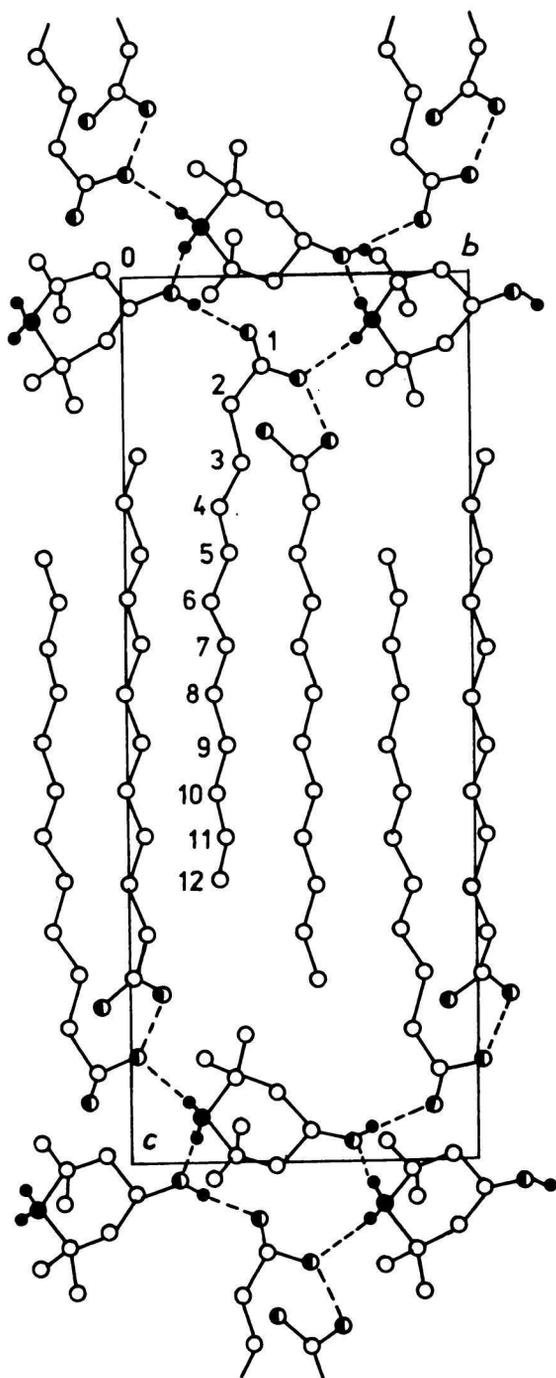


Fig. 6. Projection of the structure of the salt of TMP with dodecanoic acid. Denotation is the same as in Fig. 3.



It is noticeable that though using different ratios of TMP and octadecanoic acid for preparation of the salt, the resulting structure is always the same. Even in the case of large excess of TMP ($n(\text{TMP}) : n(\text{acid}) = 3 : 1$) the salt obtained has the same structure as described above, *i.e.* where the ratio $n(\text{TMP}) : n(\text{acid})$ is 1 : 2.

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