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THERMAL OXIDATIVE DESTRUCTION OF ISOMERIC DIPYRROLYLMETHANES

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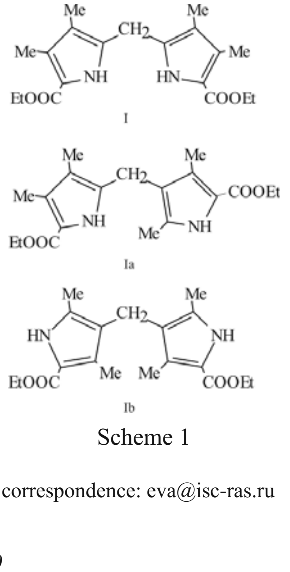
3,3',4,4'-tetramethyl-5,5'-dicarboethoxydipyrrolylmethane-2,2' and its α,β and β,β' isomers were synthesized. The compounds were characterized by recording of their proton NMR spectra. The thermal oxidative destruction of the compounds was studied by thermogravimetry. The thermal stability of dipyrrolylmethanes was found to be primarily characterised by molecular isomerism for symmetrically substituted α,α'- and β,β'-dipyrrolylmethanes compared with α,β isomer.

Keywords: *dipyrrolylmethanes, isomerism, thermal oxidative destruction, thermogravimetric method*

Introduction

Linear pyrroles play an important role in animate nature as precursors of porphyrins and related substances. In the synthetic chemistry of porphyrins and related compounds, oligopyrroles are of special interest [1, 2]. The synthesis of porphyrin-like compounds is as a rule performed at elevated temperatures, when resinification of intermediate compounds is accelerated. This decreases the yield of the desired products. For this reason, data on the stability of dipyrrolylmethanes in spite of thermal oxidative destruction are of certain interest.

The most widespread and thoroughly studied compounds of this class are 2,2'-dipyrrolylmethanes (α,α'-isomers), whereas the other isomers (α,β and β,β') have been studied to a much lesser extent [3]. This prompted us to undertake a thermogravimetric study of the thermal oxidative destruction of 3,3',4,4'-tetramethyl-5,5'-dicarbethoxydipyrrolylmethane-2,2' (I) and its α,β (Ia) and β,β' (Ib) isomers.



Scheme 1

Experimental

Materials and methods

Dipyrrolylmethanes were repared as follows: 3,3',4,4'-tetramethyl-5,5'-dicarboethoxydipyrrolylmethane-2,2' (I) was synthesized according to [3], the yield being 56%. The proton NMR spectrum (δ, pm) were: 9.56 s (1H, NH); 4.07 q (4H, CH_2-CH_3); 3.70 s (2H, ms-H); 2.12 s (6H, 4,4'-CH_3); 1.87 s (6H, 2,2'-CH_3); 1.30 t (6H, CH_2-CH_3).

3,2',4,4'-tetramethyl-5,5'-dicarboethoxydipyrrolylmethane-2,3' (Ia). A mixture of 2,2-dimethyl-5-carboethoxypyrrole (1 g, 0.6 mmol) and 3,4-dimethyl-2-acetoxymethyl-5-carboethoxypyrrole [4] (1.43 g, 0.6 mmol) in methanol (30 mL) containing HBr (0.5 mL) was heated up to boiling in a reflux condenser 1 h. The reaction mixture was then cooled, the precipitate being separated by filtration, washed with methanol, and recrystallized two times from ethanol. The yield was 65%. The proton NMR spectrum (δ, pm) were as follows: 8.78 bs (1H, NH); 8.14 bs (1H, NH); 4.24 m (4H, CH_2-CH_3); 3.63 s (2H, ms-H); 2.24 s (3H, 4-CH_3); 2.17 s (3H, 4'-CH_3); 2.14 s (3H, 2'-CH_3); 1.97 s (3H, 3-CH_3); 1.35 m (6H, CH_2-CH_3).

2,2',4,4'-tetramethyl-5,5'-dicarboethoxydipyrrolylmethane-3,3' (Ib). Paraform (0.1 g) and HBr (0.5 mL) were added to 2,4-dimethyl-2-acetoxymethyl-5-carbethoxypyrrole (1 g, 6 mmol) in ethanol (20 mL). The mixture was heated up to boiling in a reflux condenser for 1 h, with caused solution of paraform. The solution was cooled and filtered, the precipitate being washed with small amount of ethanol and dried. The yield was 65%. The proton NMR spectrum (δ, pm) were: 8.52 bs (1H, NH); 4.27 q (4H, CH_2-CH_3);

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Table 1 Thermal oxidative destruction of compounds I–III

Compound	T_{fus}/°C	$\Delta_{fus}H$/kJ mol^{-1}	T_b/°C	T_{max1}/°C	T_{max2}/°C	T_f/°C
(I)	200	49±2	228	328	478	575
(Ia)	178	18±1	210	302	473	540
(Ib)	242	44±1	260	366	532	596
(II) [10]	129	37±2	240	330	518	600
(III) [12]			190		500	560

T_{fus} is the temperature of substance fusion; $\Delta_{fus}H$ is the enthalpy of fusion; T_b, T_{max1}, and T_{max2} are the temperatures of the beginning of destruction and exothermic effect maxima; and T_f is the temperature of process completion

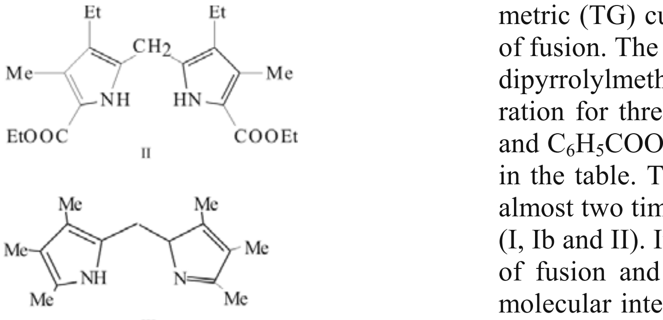
3.45 s (2H, ms-H); 2.18 s (6H, 4,4'-CH_3); 2.04 s (6H, 2,2'-CH_3); 1.33 t (6H, CH_2-CH_3).

The proton NMR spectra were recorded in $CDCl_3$ on a Bruker 200 spectrometer with tetramethylsilane as an internal reference. Thermogravimetric measurements were performed on a 1000D Derivatograph (MOM, Hungary) over the temperature range 19–1000°C; the heating rate being 5 K min^{-1}. The I, Ia and Ib sample mass was 17–19 g in separate experiments. Before measurements, the samples had been ground and in a vacuum at 350 K up to constant mass.

Results and discussion

According to [6], pyrrole undergoes oxidation under the air and light with the formation of colored products such as: oxopyrrolines, di- and trimeric pigments. The rate of pyrrole oxidation increases in the presence of alkyl substituents in its aromatic ring. It should be noted that dipyrrolylmethanes are stable only in the presence of electron acceptor groups in their molecules. In the absence of such groups, they are easily oxidized to the corresponding dipyrrolylmethenes. The quantitative characteristics of thermal oxidative destruction and the literature data on the compounds are listed in Table 1. The derivatograms of I, Ia and Ib are shown in Figs 1–3.

The thermal oxidative destruction of dipyrrolylmethanes begins at 210–260°C. At higher temperatures, the differential thermal analysis (DTA) curves contain several (as a rule two) exothermic peaks corresponding to deeper oxidation and burning processes. The pyrolysis of these compounds stops at 500–600°C, being accompanied by complete mass loss.



Scheme 2

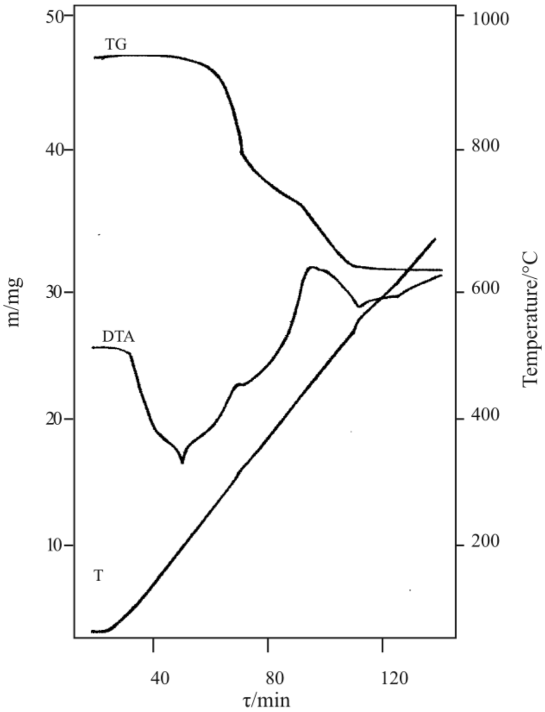


Fig. 1 TG, DTG, DTA curves of 3,3',4,4'-tetramethyl-5,5'-dicarboethoxydipyrrolylmethane-2,2'

DTA curves are found to contain an endothermic peaks at 129–242°C, it is a temperature much lower than t_b. This endothermic effect is not accompanied by mass loss, as follows from the thermogravimetric (TG) curve. This evidences of the occurrence of fusion. The enthalpies of fusion $\Delta_{fus}H$, kJ mol^{-1}, of dipyrrolylmethanes calculated on the data of calibration for three reference compounds (AgS_2, KCNS and C_6H_5COOH) as recommended in [7–9] are listed in the table. The $\Delta_{fus}H$ value is minimum for Ia and almost two times higher for the α,α' and β,β' isomers (I, Ib and II). It can be suggested that the temperature of fusion and the $\Delta_{fus}H$ value are related to intermolecular interaction in crystals and the special features with respect to each other, due to the isomerism

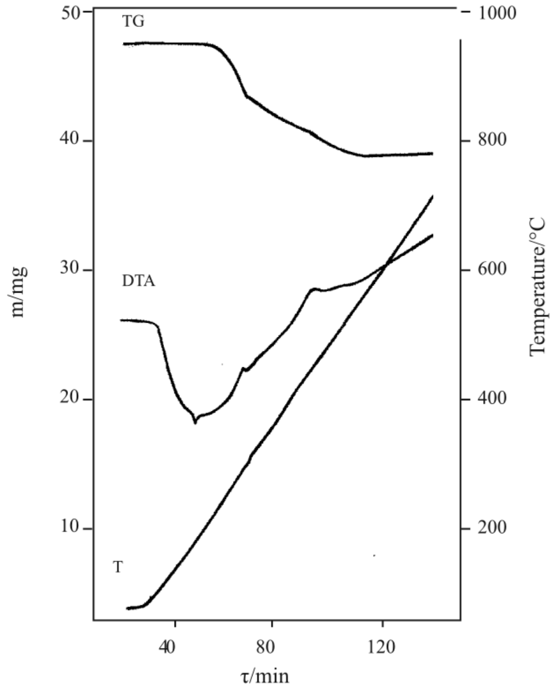


Fig. 2 TG, DTG, DTA curves of 3,2',4,4'-tetramethyl-5,5'-dicarboethoxydipyrrolylmethane-2,3'

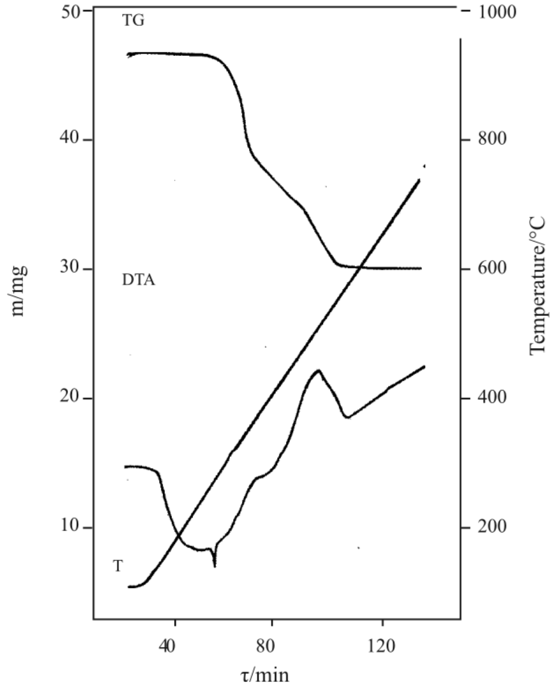


Fig. 3 TG, DTG, DTA curves of 2,2',4,4'-tetramethyl-5,5'-dicarboethoxydipyrrolylmethane-3,3'

type. The analysis of temperatures at the beginning of destruction (t_b) shows that isomerism substantially influences the stability of dipyrrolylmethanes thermal oxidation. The transition from the α,β to α,α' and β,β' isomers is accompanied by increase of thermal stability (by 18–20 K), isomer being the most stable.

A comparison of the data 3,3',4,4'-tetramethyl-5,5'-dicarboethoxydipyrrolylmethane-2,2' (I) with the literature data [10] on 3,3'-dimethyl-4,4'-diethyl-5,5'-dicarboethoxydipyrrolylmethane-2,2' (II) shows that the thermal stability of the latter is decreased by 12 K because of the introduction of ethyl groups into the position 4 and 4'. A similar decrease in the thermal stability of polypyrroles while the length of functional substituents increased was observed in [11]. 3,3',4,4',5,5'-hexamethyldipyrrolylmethane-2,2' (III) [12] is less stable compared with the 'reduced' analogues of dipyrrolylmethane I. The transition from dipyrrolylmethane to dipyrrolylmethenes is accompanied by the formation of an extended system of π bonds because of the conjugation of the aromatic π systems of pyrrole rings as a result of the dehydrogenation of the methylene bridge. Because of this structural feature, alkyl derivatives of dipyrrolylmethenes undergo oxidation more readily than dipyrrolylmethanes.

To summarize, the dipyrrolylmethane isomers studied can be characterized as stable organic compounds whose thermal stability decreases in the series β,β'>α,α'>α,β and is higher than that of unsaturated unstabilized dipyrroles.

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