

# Hydroxyalkylation of Parabanic Acid. I. Reactions with Formaldehyde

IWONA ZARZYKA-NIEMIEC, JACEK LUBCZAK

Rzeszów University of Technology, Faculty of Chemistry, 35-959 Rzeszów, Poland

Received 9 January 2001; accepted 18 July 2001

**ABSTRACT:** The results of investigations into the reaction of parabanic acid with formaldehyde at different molar ratios of the reagents are presented. A fast and effective method of synthesis of *N,N'*-bis(hydroxymethyl)parabanate was developed. The reaction of parabanic acid with an excess of formaldehyde was analyzed and the structure of the products proposed. Conditions at which the hydroxymethyl derivatives of parabanic acid undergo self-condensation as well as prospects of using them in subsequent oxyalkylation with oxiranes are specified. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2858–2872, 2002; DOI 10.1002/app.10274

**Key words:** parabanic acid; formaldehyde; addition polymerization; structure of products

## INTRODUCTION

Parabanic acid (1,3-imidazolidine-2,4,5-trione) is a crystalline solid melting at 242–243°C with decomposition.<sup>1</sup> It is soluble in water, warm ethanol,<sup>2</sup> methanol, *N,N*-dimethylformamide, or dimethyl sulfoxide. It crystallizes reasonably only from water. It is a dibasic acid with ionization constants of  $6.0 \times 10^{-7}$  and  $1.6 \times 10^{-11}$ .<sup>3</sup> A high decomposition temperature of parabanic acid makes it an interesting starting material in the synthesis of polymeric materials of improved thermal stability. Interest in applying this compound in polymer synthesis has so far been minimal. We have found only a note on the application of *N,N'*-diglycidyl parabanate as a component of crease-proof preparations for cotton fabrics.<sup>4,5</sup> Polymers with parabanic acid rings were obtained in the reactions of dicyanoforamides with appropriate diisocyanates.<sup>6</sup> Polymerization of cyanoforamidyl isocyanate that contains a parabanic acid ring in its structure was

also carried out.<sup>7</sup> The structure and properties of poly(parabanic acid) were recently described.<sup>8</sup>

We have found no information on the hydroxyalkylation of parabanic acid. Such a reaction should lead to the respective *N,N'*-bis(hydroxyalkyl) and *N,N'*-bis(hydroxyalkoxyl) derivatives. These compounds have been expected to react with epoxy resins to yield products of improved thermal stability.

We initiated an investigation aimed at the hydroxyalkylation of parabanic acid with formaldehyde, selected oxiranes, or alkyl carbonates. In this report, we present the results obtained by reacting parabanic acid with formaldehyde. Similar reactions were studied by Oda and Baba<sup>9</sup> in the 1960s and also by Cassidy et al. in the 1980s.<sup>10</sup> By reacting 1 mol of formaldehyde with 1 mol of parabanic acid, Oba and Baba obtained *N*-(hydroxymethyl)hydroparabanate, which crystallized as a monohydrate and melted at 142°C. Cassidy et al. did not confirm this result and obtained a product of a reaction of parabanic acid with 2 mol of formaldehyde at room temperature, which melted at 130°C. Attempts of polymerizing the derivative by keeping it for 16 h at 50–60°C led to a product that was insoluble in organic

Correspondence to: J. Lubczak.

*Journal of Applied Polymer Science*, Vol. 83, 2858–2872 (2002)  
© 2002 John Wiley & Sons, Inc.

solvents, but soluble in *N,N*-dimethylformamide. Prolonged heating at a temperature elevated to 90°C yielded a product insoluble in any solvent.<sup>10</sup>

## EXPERIMENTAL

### Syntheses

#### *Reactions of 1 Mol of Parabanic Acid with 2 Mol of Formaldehyde*

Parabanic acid (5.7 g, 0.05 mol) prepared directly from urea (POCH, Gliwice, Poland) and diethyl oxalate (pure, Fluka, Buchs, Switzerland)<sup>11</sup> was placed in a 200-cm<sup>3</sup> beaker with formalin solutions (pure, POCh, Gliwice, Poland) in amounts to contain 0.1 mol of formaldehyde [Note (a) below]. Various amounts of a triethylamine (pure, Fluka, Switzerland) catalyst (0–18 cm<sup>3</sup>/mol of parabanic acid) were added. Parabanic acid dissolved in the solutions and then a solid precipitated at different rates, depending on the formaldehyde concentration [Note (b) below]. The reactions were carried out at room temperature or at 80°C until the reaction mixture solidified. The product was purified by crystallization from ethyl acetate (cf. Table I, runs 2–8).

Notes:

- (a) Formalin containing about 36 wt % of formaldehyde and diluted formalin of a concentration of 10–14 wt % of formaldehyde were used.
- (b) Rapid dissolution of parabanic acid took place in the presence of the triethylamine catalyst as well as in concentrated formalin.

#### *Reactions of Parabanic Acid with Excess of Formaldehyde*

Parabanic acid (0.05 mol; 5.7 g) was placed in a 200-cm<sup>3</sup> beaker to which formaldehyde was introduced in amounts sufficient to yield a molar ratio of reagents equal to 1:3, 1:4, or 1:5. The reaction was carried out at room temperature or at 80°C. When the reaction was carried out at room temperature, slow precipitation of a solid was observed, and a rapid precipitation of the product was observed when the triethylamine catalyst was used. The precipitate was filtered off, washed with acetone or ethyl acetate, and dried to a constant weight at 40°C under reduced pressure. For the reaction carried out at 80°C, no precipitate formation was observed. The reaction mixture

was cooled and water was distilled off at a reduced pressure ( $p = 15$  mmHg/20 hPa) at a temperature below 60°C (cf. Table I, runs 9–14).

#### *Attempts of Polymerization of Hydroxymethyl Derivatives of Parabanic Acid*

Attempts of the polymerization of parabanic acid and its derivatives were carried out at the following molar ratios of the reagents (cf. Table II):

- At a molar ratio of parabanic acid to formaldehyde of 1:1, the latter in the form of a dilute aqueous solution (~1.5 wt %) at room temperature;
- As above, but at 50–90°C and a slightly higher content of formaldehyde in formalin (~2 wt % of CH<sub>2</sub>O).

The reactions were carried out in a 200-cm<sup>3</sup> beaker at room temperature or in a three-necked round-bottomed flask equipped with a mechanical stirrer and reflux for the reaction carried out at elevated temperature. The total amount of the reagents was each time the same and equal to 0.05 mol. Initially, the reactions were carried out without a catalyst and then acidic or basic catalysts were used. To the *N,N'*-bis(hydroxymethyl)parabanate obtained as described in the section Reactions of 1 Mol of Parabanic Acid with 2 Mol of Formaldehyde and dissolved in water without isolation, sulfuric acid (98 wt %) or a sodium hydroxide aqueous solution (30 wt %) was gradually added until a precipitate appeared.

#### *Parabanic Acid–Triethylamine Adduct (Triethylammonium Hydroparabanate)*

The adduct was obtained at room temperature by adding, while stirring, 0.05 mol of triethylamine to 0.05 mol of parabanic acid dissolved in 150 cm<sup>3</sup> of THF. The resulting precipitate was filtered off and washed with acetone and dried at room temperature to obtain a crystalline solid of mp 149–150°C.

#### Analytical Methods

The content of hydroxymethyl groups (labile formaldehyde) in the products of the reaction of parabanic acid with formaldehyde was calculated from iodometric analysis and from acid number determination.<sup>12</sup> <sup>1</sup>H-NMR spectra of the products were recorded at 25°C in *d*<sub>6</sub>-DMSO on an FT <sup>1</sup>H-NMR spectrometer BS 587A (80 MHz, Tesla,

**Table I** Conditions of Reaction of Parabanic Acid (PA) with Formaldehyde and Some Properties of Products

Run	PA : CH <sub>2</sub> O Molar Ratio	Amount of Water <sup>a</sup> (g/mol PA)	Amount of Et <sub>3</sub> N (cm <sup>3</sup> / mol PA)	Temper- ature (°C)	Time of Reaction (min)	Method of Product Separation	Appearance	Product Characteristics						
								AN (mg KOH/g)		Wt % of CH <sub>2</sub> O		PA : CH <sub>2</sub> O Molar Ratio in Product	Melting Point (°C)	Yield (%)
								Calcd <sup>b</sup>	Found	Calcd	Found			
1	1 : 2,2	500	—	25	120 h	Crystallization from methanol	White precipitate	312	363	36.6	26.4	1 : 1.4	124	43
2	1 : 2	480	18	25	39 h	Crystallization from ethyl acetate	As above	322	278	34.5	28.9	1 : 1.6	132	17
3	1 : 2	—	10	25	8	As above	As above	322	321	34.5	34.4	1 : 2	133	51
4	1 : 2	—	6	25	8	As above	As above	322	321	34.5	34.4	1 : 2	131	70
5	1 : 2	—	4	25	8	As above	As above	322	320	34.5	33.5	1 : 2	130	86
6	1 : 2	—	2	25	8	As above	As above	322	320	34.5	33.4	1 : 2	131	92
7	1 : 2	—	—	25	8	As above	As above	322	326	34.5	34.4	1 : 2	132	93
8	1 : 2,4	—	18	25	8	As above	As above	302	325	38.7	35.0	1 : 2	135	72
9	1 : 3	—	2	25	8	As above	As above	275	320	44.1	34.3	1 : 2	132	72
10	1 : 4	—	7.6	25	8	As above	As above	240	326	51.3	35.7	1 : 2	132	70
11	1 : 5	—	3.8	25	8	As above	As above	213	323	56.8	35.3	1 : 2	132	76
12	1 : 2	—	—	80	300	As above	As above	322	323	34.5	34.4	1 : 2	134	93
13	1 : 4	—	7.6	80	240	Water distilled off	Thick white resin	240	222	51.3	43.6	1 : 3	—	91
14	1 : 5	—	6.5	80	210	Water distilled off	Thick opaque resin	213	200	56.8	51.2	1 : 4	—	96

<sup>a</sup> On top of water introduced with formalin (36 wt % of CH<sub>2</sub>O).<sup>b</sup> Calculated from the initial mixture composition.

**Table II Polymerization of Hydroxymethyl Derivatives of Parabanic Acid (PA) and Some Properties of Products**

Run	Initial PA : CH <sub>2</sub> O Molar Ratio	Amount of Water <sup>a</sup> (g/mol PA)	Amount of Catalyst (cm <sup>3</sup> /mol KP)	Temperature (°C)	Time of Reaction	Method of Product Separation	Product Characteristics			
							Product Appearance	Wt % of CH <sub>2</sub> O		Actual PA : CH <sub>2</sub> O Molar Ratio
							Calcd <sup>b</sup>	Found		
1	1 : 2	—	1 cm <sup>3</sup> concentrated H <sub>2</sub> SO <sub>4aq</sub>	80	180 min	Washed with acetone	White precipitate	34.5	28.1	1 : 1.6
2	1 : 2	—	As above	As above	30 min	As above	As above	As above	27.9	As above
3	1 : 1	—	10 cm <sup>3</sup> TEA <sup>c</sup>	Room	5 min	Crystallized from ethyl acetate	As above	20.8	22.5	1 : 1.3
4	1 : 1	2000	—	As above	12 days	Crystallized from methanol	White sticky precipitate	As above	14.7	1 : 0.71
5	1 : 1	1380	—	50–90	24.5 h	Washed with water	White precipitate	As above	5.80	1 : 0.29
6	1 : 1	1430	—	85	26 h	As above	As above	As above	6.15	1 : 0.30

<sup>a</sup> On top of water introduced with formalin (36 wt % of CH<sub>2</sub>O).

<sup>b</sup> The content of formaldehyde was calculated assuming the composition of derivative corresponds to the initial molar ratio of the reagents.

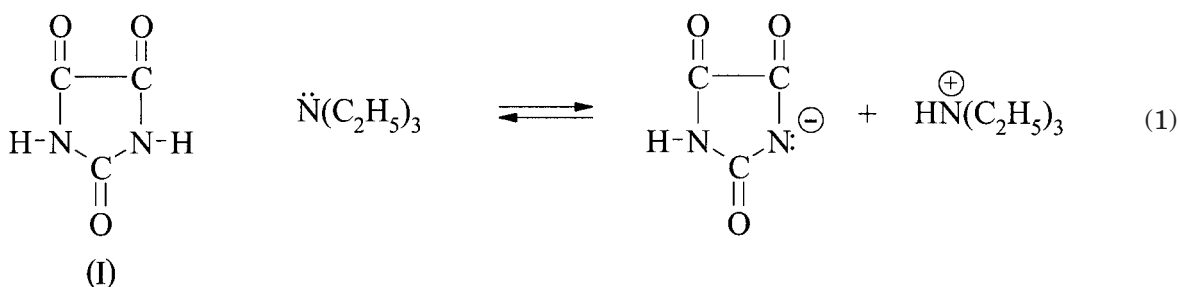
<sup>c</sup> TEA: triethylamine.

Czechoslovakia). IR spectra were recorded from a capillary film or KBr pellets on a PARAGON 1000 FT spectrometer (Perkin-Elmer). Elemental analysis (EA 1108, Carlo-Erba analyzer) and thermal analysis (Paulik-Paulik-Erdey derivatograph, MOM, Hungary) were also made. The specific conductivity of the reaction mixtures in water containing parabanic acid and triethylamine was measured conductometrically (OK-102/1 conductometer, Radelkis, Hungary) at 20°C. The system was calibrated with aqueous solutions containing various amounts of the components. The concentrations of triethylamine and parabanic acid were changed in the range of 0.00–0.25 mol/dm<sup>3</sup>. The molar ratios of the components were changed with the interval of 0.1 mol/mol.

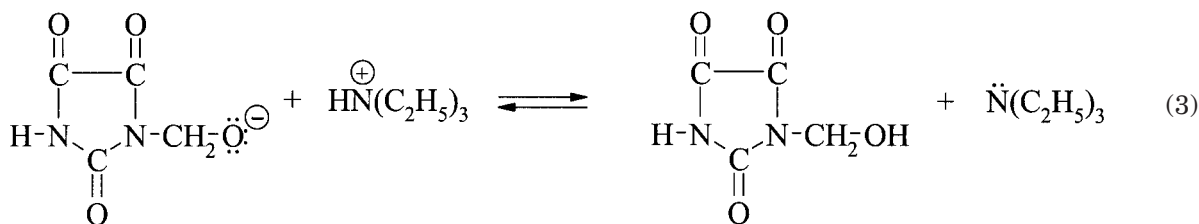
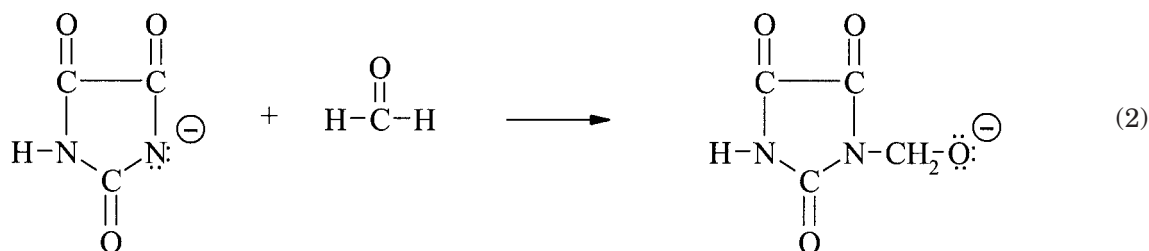
## RESULTS AND DISCUSSION

### Synthesis of *N,N'*-Bis(hydroxymethyl)parabanate

Cassidy et al.<sup>10</sup> carried out the synthesis in a dilute aqueous solution of parabanic acid and formaldehyde (ca. 9 wt % of CH<sub>2</sub>O) at room temperature. They applied a quite complicated procedure of recovering the product that consisted of evaporating the solvent for 12 days under reduced pressure. In this work, we added the triethylamine catalyst to speed up the reaction (Table I, run 2). We expected amine to create a nucleophilic site at the nitrogen atom of parabanic acid (**I**) that would attract the formaldehyde carbonyl more strongly than the acid itself:



(I)



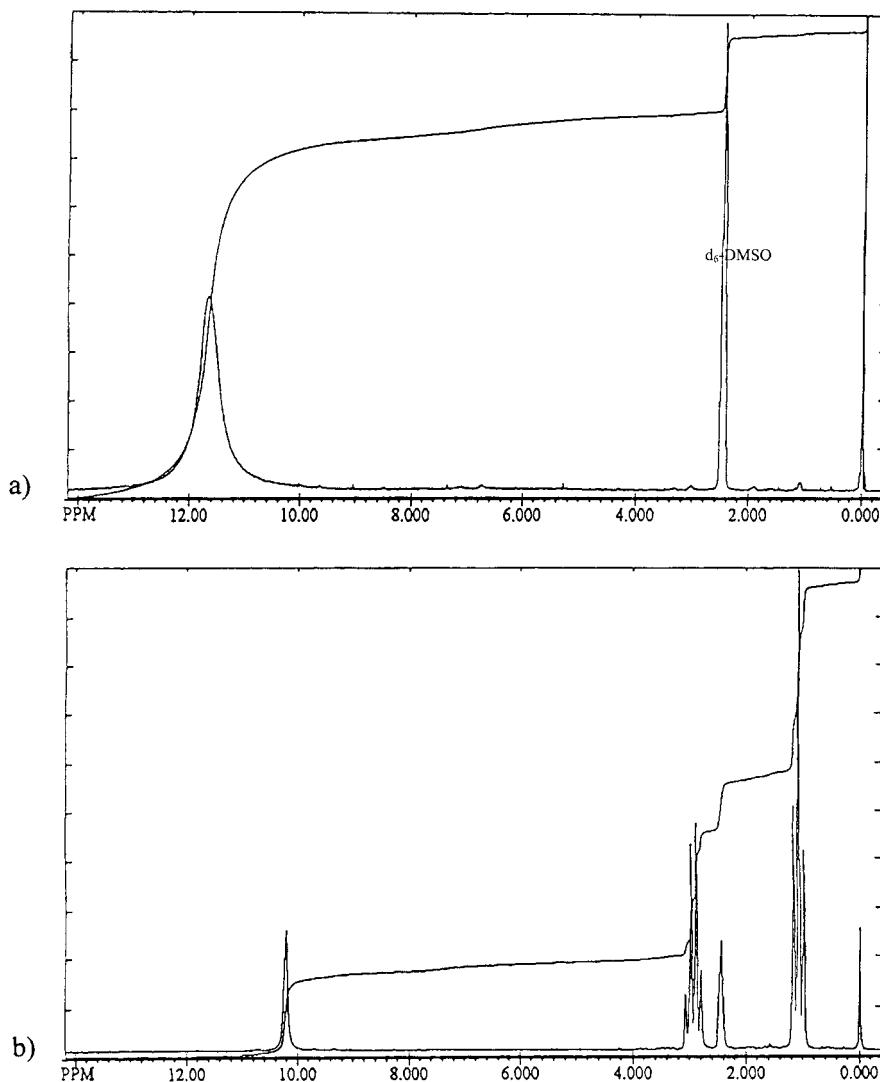
This mechanism of reaction seems to be correct since a parabanic acid/triethylamine adduct was formed. Its presence was proved in three ways:

- In the <sup>1</sup>H-NMR spectrum [Fig. 1(a)], the chemical shift due to —NH protons of parabanic acid is 11.7 ppm, while for the mixture,

it is 10.2 ppm [Fig. 1(b)], suggesting that an ion pair or even free ions are formed;

- In the IR spectrum [Fig. 2(b)], medium-intensity bands appear at about 2500 cm<sup>-1</sup> ascribed to vibrations of an  $\overset{\oplus}{\text{N}}-\text{H}$  group;





**Figure 1**  $^1\text{H-NMR}$  spectrum (a) of parabanic acid and (b) of its adduct with triethylamine dissolved in  $d_6$ -DMSO.

- A band at  $1588\text{ cm}^{-1}$  also appears that does not exist in the spectrum of pure parabanic acid [Fig. 2(a)] and comes from vibrations of  $-\text{C}=\text{N}-$  groups, suggesting, partially at least, enolization of the acid.

The adduct consists of one parabanic acid molecule and one triethylamine molecule. This can be established by measuring the conductivity of aqueous solutions of the reagents carried out at different initial molar ratios (Fig. 3). The highest conductivity is obtained in solutions where the ratio is 1:1. Hence, depending on the polarity of the system, triethylammonium hydroparabanate may assume the form of an ion pair of free ions.

As follows from the preliminary results, triethylamine accelerates the reaction of parabanic acid with formaldehyde. In the synthesis carried out according to the procedure published by Cassidy et al.,<sup>10</sup> (Table I, run 1) precipitation of  $N,N'$ -bis(hydroxymethyl)parabanate was observed after about 2.5 h. In the presence of triethylamine, precipitation occurred after a much shorter time of about 30 min. Next, attempts were made using formalin containing about 36% of formaldehyde. No effect of the catalyst on the reaction rate was observed in these cases (Table I, runs 3–6). When standard formalin was used, the precipitate formation was pretty rapid. It appeared at room temperature after about 8 min (Table I, run 7). An

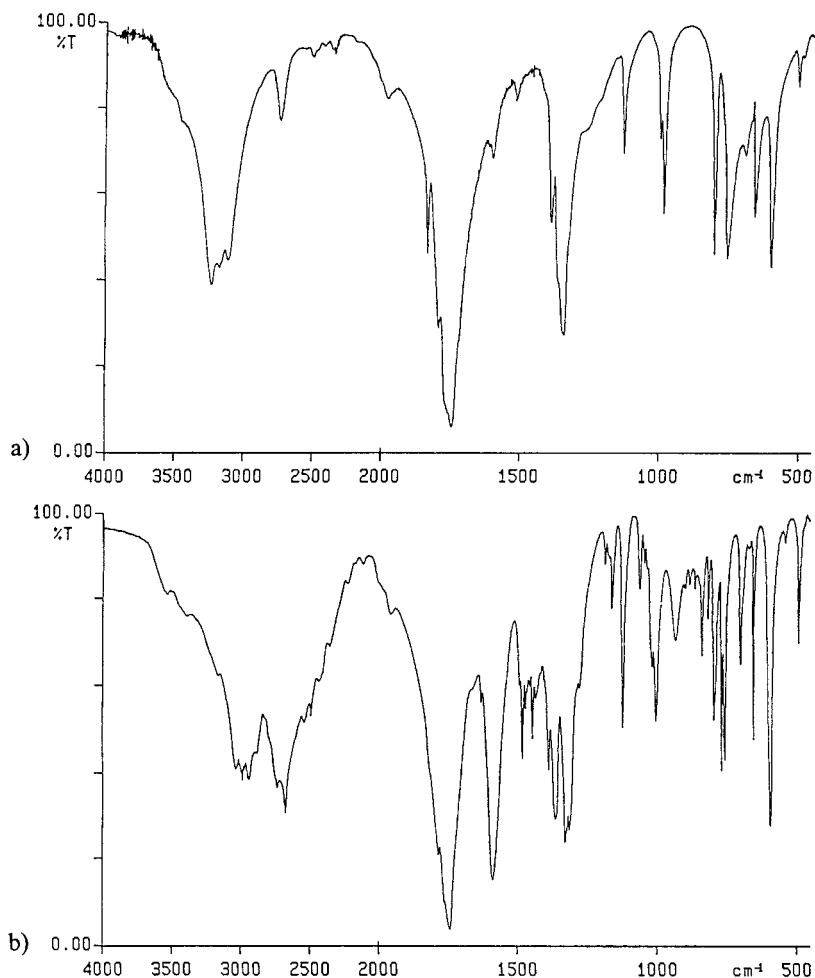


Figure 2 IR spectrum (a) of parabanic acid and (b) of its adduct with triethylamine.

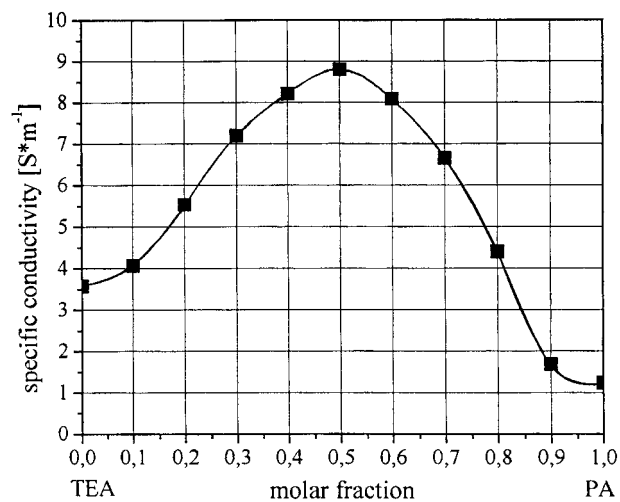


Figure 3 Specific conductivity versus molar fraction of parabanic acid (PA) and triethylamine (TEA).

increase in formaldehyde excess from the molar ratio of parabanic acid to formaldehyde of 1:2.4–1:5 did not result in the formation of other products at room temperature than *N,N'*-bis(hydroxymethyl)parabanate (Table I, runs 8–11). The mixture of the molar ratio of 1:2 kept for several hours at elevated temperature (80°C) also produced the same product (Table I, run 12), which was confirmed by spectral (IR and <sup>1</sup>H-NMR) and elemental analyses as well as by the determination of the labile formaldehyde content in the product.

*N,N'*-Bis(hydroxymethyl)parabanate dissociates in an aqueous solution, releasing formaldehyde. The latter can easily be determined iodometrically. The analysis gives a result consistent with structure (II) of the product (% CH<sub>2</sub>O<sub>calcd</sub> = 34.5, % CH<sub>2</sub>O<sub>found</sub> = 34.4):

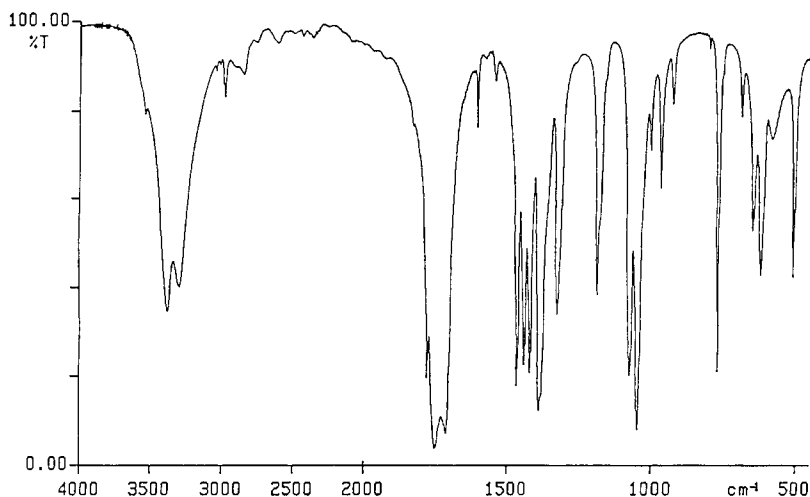
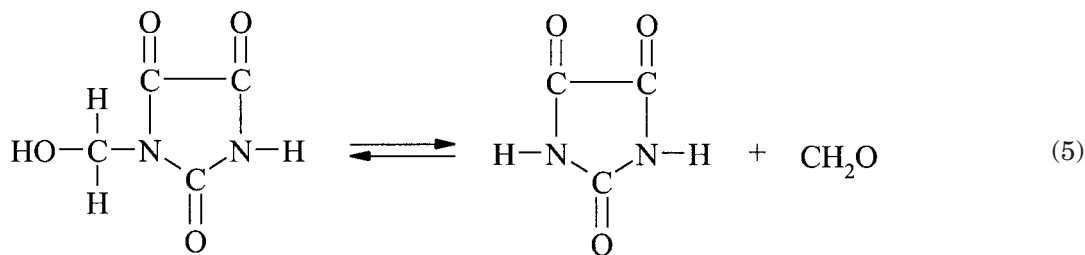
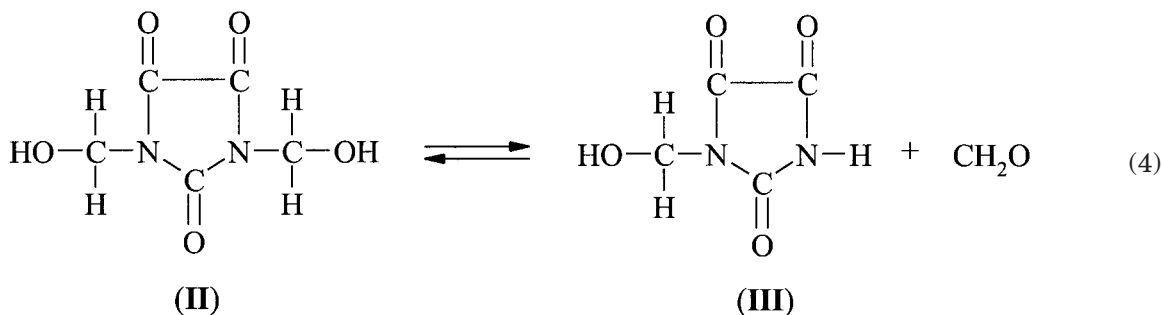


Figure 4 IR spectrum of *N,N'*-bis(hydroxymethyl)parabanate.



Pure parabanic acid in aqueous solutions behaves as a monobasic acid. Titrated with 0.1M KOH<sub>aq</sub>, it returns to the acid number (AN) equal to 492.5 mg KOH/g (AN<sub>calcd</sub> = 492.1 mg KOH/g). Assuming that just one formaldehyde molecule dissociates from *N,N'*-bis(hydroxymethyl)parabanate, leaving a monobasic acid behind, the acid number should be AN<sub>calcd</sub> = 322.4 mg KOH/g. The experimental value was found, indeed, to be AN<sub>found</sub> = 320–327 mg KOH/g.

The course of the reaction between parabanic acid and formaldehyde was followed using spectral analyses (<sup>1</sup>H-NMR and IR). In the IR spec-

trum of pure parabanic acid [Fig. 2(a)], characteristic bands can be seen at 3100–3300 cm<sup>-1</sup> from valency vibrations of —NH groups as well as at 1388, 1130, and 985 cm<sup>-1</sup> from deformational vibrations of these groups. A strong band at about 1745 cm<sup>-1</sup> indicates the solid acid to be in the ketone form. In the spectrum of *N,N'*-bis(hydroxymethyl)parabanate (Fig. 4), the bands due to deformational vibrations of —NH groups are absent, the shape of the bands above 3000 cm<sup>-1</sup> is changed, and the carbonyl group band is still present. A band appears at 1070 cm<sup>-1</sup> due to deformational vibrations of the hydroxyl group.



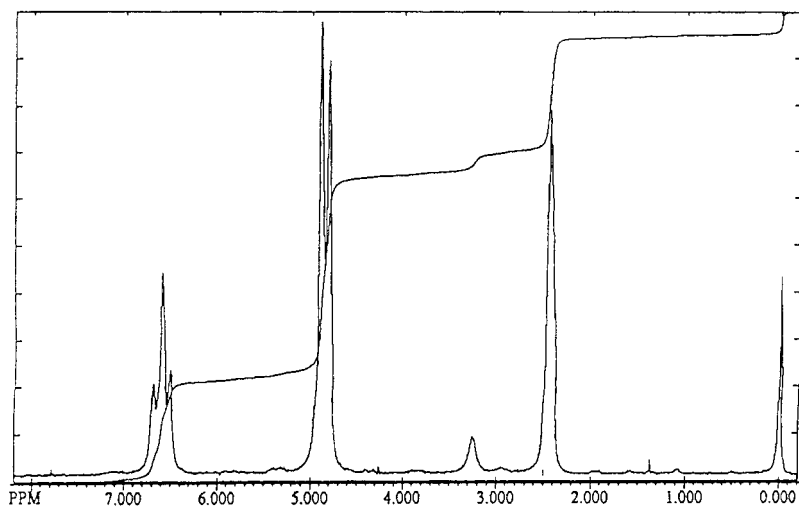


Figure 5  $^1\text{H-NMR}$  spectrum of  $N,N'$ -bis(hydroxymethyl)parabanate.

The spectra suggest that formaldehyde reacts with the nitrogen atom and not with the enolic oxygen of parabanic acid, as Cassidy et al. suggested.<sup>10</sup> No band was found in the IR spectra at about  $1588\text{ cm}^{-1}$  due to  $-\text{C}=\text{N}-$  groups that should be present in an enolic form of the acid.

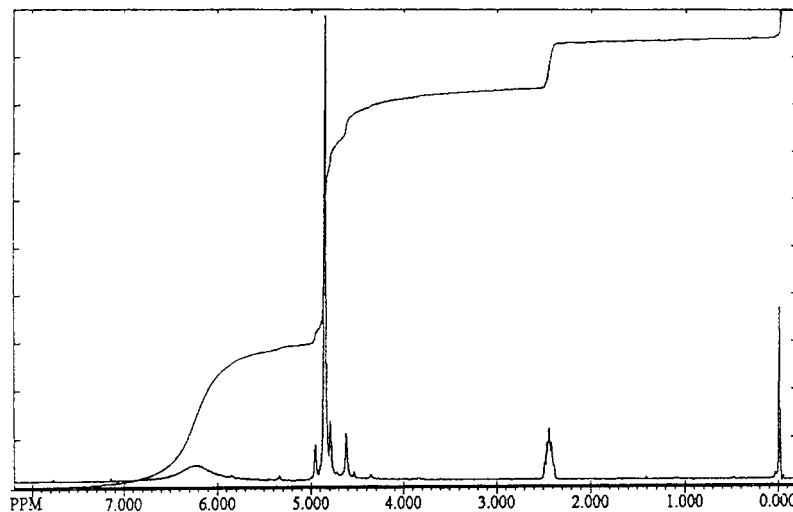
Further evidence is provided from the  $^1\text{H-NMR}$  spectra of the products (Fig. 5). Two signals are present: a triplet at 6.6 ppm from protons in the hydroxyl groups and a doublet at 4.8 ppm from methylene protons. The ratio of the areas under the bands is 1:2, as expected for  $N,N'$ -bis(hydroxymethyl)parabanate. No signals from unreacted imide groups were found in the spectra. The band at 6.6 ppm vanishes when heavy water is added to the system. This proves that it comes from OH groups. The evidence that  $N$ -hydroxymethyl, rather than  $O$ -hydroxymethyl, is formed is provided by the signal at 4.85 ppm. In refs. 13 and 14, we showed this shift to be typical for methylene group protons in a  $-\text{N}-\text{CH}_2-\text{OH}$  grouping. Elemental analysis provided yet more evidence that the product was  $N,N'$ -bis(hydroxymethyl)parabanate (%  $C_{\text{calcd}} = 34.48$ ; %  $C_{\text{found}} = 34.88$ ; %  $H_{\text{calcd}} = 3.45$ ; %  $H_{\text{found}} = 3.52$ ; %  $N_{\text{calcd}} = 16.09$ ; %  $N_{\text{found}} = 16.47$ ).

In concluding, one should point out that the synthesis of  $N,N'$ -bis(hydroxymethyl)parabanate can be made considerably shorter than 12 days.<sup>10</sup> In fact, it can be completed within several minutes and avoid water evaporation since the product precipitates in the form convenient for washing and recrystallization. The yield of the synthe-

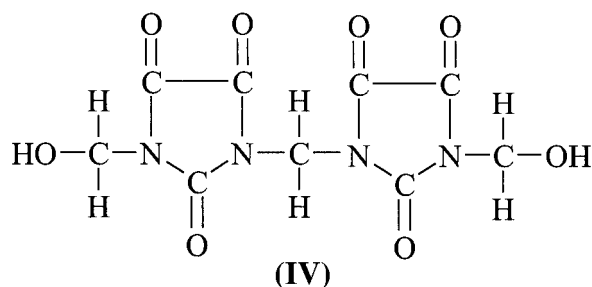
sis reaches 93%, some 1.5 times more than in Cassidy et al.'s experiments. Ethyl acetate has been found to be a convenient solvent in the crystallization of the product, much better than methanol as suggested by Cassidy et al.,<sup>10</sup> which required preevaporation before the product crystallized. We found beyond doubt that, in the product of the reaction of formaldehyde with parabanic acid, hydroxymethyl groups are linked to nitrogen atoms. It seems worth noting that a lengthy synthesis (lasting several days) is not favorable since hydroxymethyl groups may condense to form dimethylene-ether bridges. In the  $^1\text{H-NMR}$  spectra of such products, a weak band at 4.50 ppm was present. On the other hand, a large excess of formaldehyde (much more than 2 mol per mol of parabanic acid) leads to a product containing a small amount of hemiacetal groups ( $-\text{O}-\text{CH}_2-\text{OH}$ ) that produce a weak peak at 4.65 ppm.

#### Reactions of Parabanic Acid with Excess of Formaldehyde

A lengthy reaction carried out at the molar ratio of reagent 1:2.2 in diluted formaldehyde (9 wt %) resulted in partial condensation of the hydroxymethyl groups. The resulting oligomer can be extracted from the product with methanol. The acid number and formaldehyde content in the oligomer were about 370 mg KOH/g and 24 wt % of  $\text{CH}_2\text{O}$ . These figures correspond approximately to a compound of structure (IV) below:



**Figure 6**  $^1\text{H-NMR}$  spectrum of the mixture obtained in the reaction of 1 mol of parabanic acid with 2.2 mol of formaldehyde carried out for 120 h.



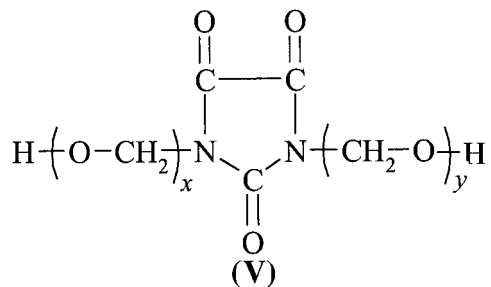
$$\% \text{CHO}_2\text{O} = 20.0$$

$$\text{AN}_{\text{calcd.}} = 374 \text{ mg KOH/g}$$

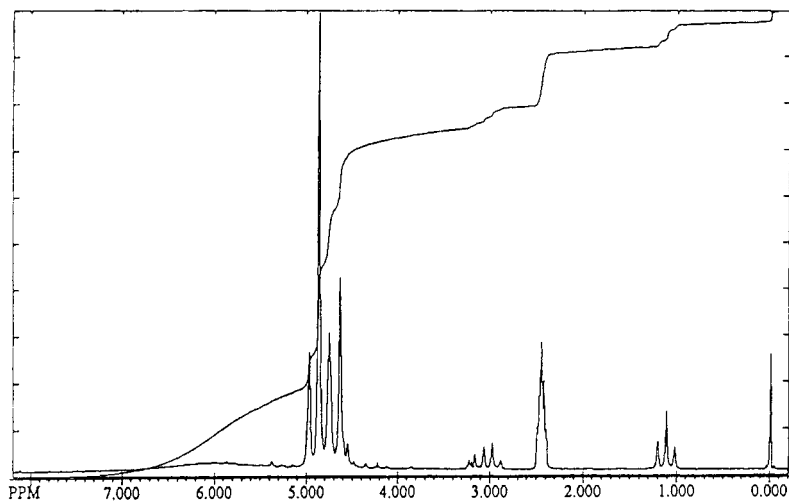
The structure was confirmed by  $^1\text{H-NMR}$  spectra of the postreaction mixture and of the product isolated from methanol. A signal at 4.75 ppm is present in the former (Fig. 6) that can be interpreted as a signal from protons in the methylene bridges of  $-\text{N}-\text{CH}_2-\text{N}-$ , linking two rings of parabanic acid. Its intensity increased in products purified by dissolving it several times in methanol (which required heating) or in the products of the reaction carried out at  $80^\circ\text{C}$ . Also, a signal at 4.5 ppm is observed in the spectrum of the postreaction mixture, which is due to the presence of dimethyl ether bridges, and a signal from *O*-hydroxymethylene protons at 4.65 ppm, indicating that a slight excess of formaldehyde is present in the system relative to the amount of imide groups.

It was also found that at the molar ratio of the reagent of 1:3 (Table 1, run 9) in the presence of

triethylamine and at room temperature *N,N'*-bis(hydroxymethyl)parabanate was formed after 8 min, but since it precipitated out, it did not react with the formaldehyde excess and no further addition products were formed. A similar situation occurred at a somewhat larger excess of formaldehyde in the starting mixture (molar ratios of 1:4 and 1:5, Table I, runs 10 and 11). At the same molar ratio of 1:4, but when the reaction is carried out at  $80^\circ\text{C}$  (Table I, run 13), *N,N'*-bis(hydroxymethyl)parabanate remained dissolved, and upon cooling and water removal, one found a resinous product of acid number 222 mg KOH/g (figure uncorrected for triethylamine presence) and a formaldehyde content of 43.6 wt %. These numbers suggest the presence of about three formaldehyde molecules per parabanic acid ring in the compound of structure (V) with  $x + y \approx 3$ :



Similar reasoning leads to the conclusion that the resinous product formed in the reaction of 1 mol of parabanic acid with 5 mol of  $\text{CH}_2\text{O}$  (Table I, run



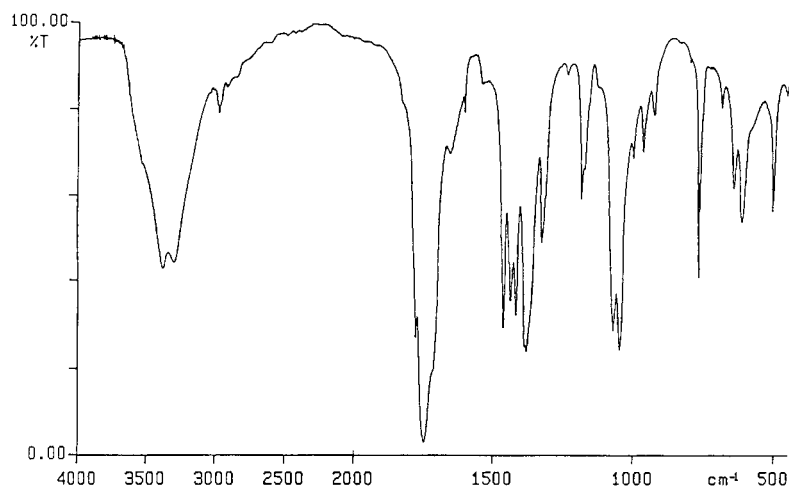
**Figure 7**  $^1\text{H-NMR}$  spectrum of reaction product of parabanic acid with formaldehyde at the molar ratio of reagents of 1:3.

14) ( $\% \text{CH}_2\text{O}_{\text{found}} = 51.2$ ;  $\text{AN}_{\text{found}} = 200 \text{ mg KOH/g}$ ) is again compound (**V**) with  $x + y \approx 4$ . In both cases, the products contain about one formaldehyde molecule less than used in the reaction. The remaining formaldehyde is removed from the system during water removal (by distilling it out). The differences in the calculated and found acid numbers are due to the presence of basic triethylamine, which forms an adduct with hydroxymethyl groups and cannot be completely removed along with water.  $^1\text{H-NMR}$  spectra of these products seemed to confirm this conclusion. Peaks at 1.1 and 3.0 ppm observed in the spectra are due to methyl and methylene protons of triethylamine,

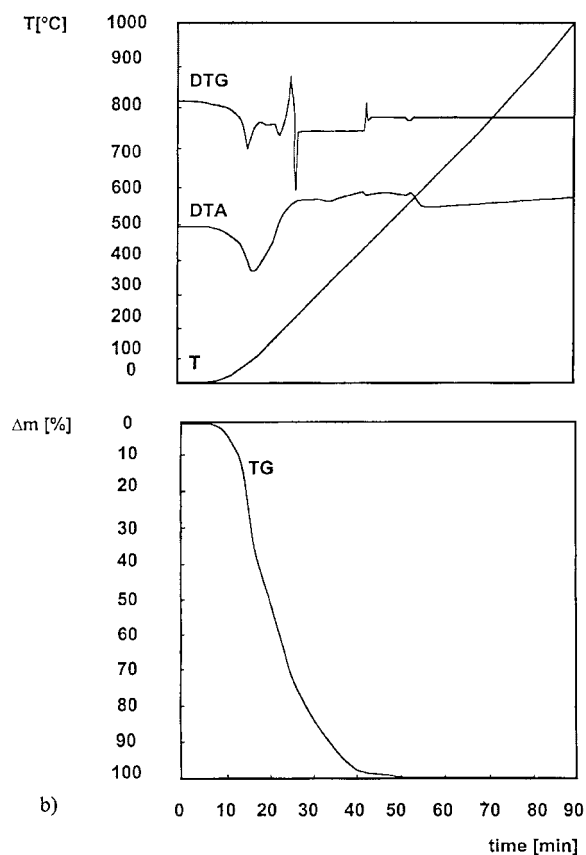
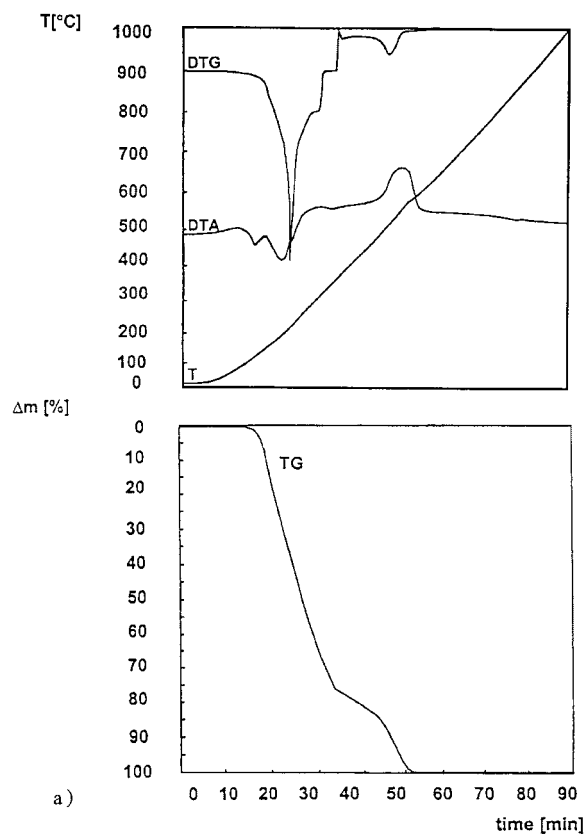
respectively (Fig. 7). The calculated acid numbers for compound **V** corrected for the presence of triethylamine (as estimated from respective  $^1\text{H-NMR}$  spectra) are  $\text{AN}_{x+y=3} = 245 \text{ mg KOH/g}$  and  $\text{AN}_{x+y=4} = 215 \text{ mg KOH/g}$ , respectively.

In the spectra of the reaction products of 1 mol of parabanic acid with 4 mol of formaldehyde, there are signals from the protons of  $-\text{N}-\text{CH}_2-\text{O}-$  grouping at 4.8–4.9 ppm, dioxymethylene bridges  $-\text{O}-\text{CH}_2-\text{O}-$  at 4.6 ppm, and a hydroxyl group at 6.0 ppm. The last vanishes as heavy water is added.

The formation of ether bridges can be traced in IR spectra of the products as well (Fig. 8). Bands



**Figure 8** IR spectrum of reaction product of parabanic acid with formaldehyde at the molar ratio of reagents of 1:3.



at 1073.9 and 1187.5  $\text{cm}^{-1}$  appear due to stretching vibrations of  $\text{—C—O—C—}$  bonds.

Parabanic acid melts with decomposition at 240°C. Its  $N,N'$ -bis(hydroxymethyl) derivative is less thermally stable than acid and starts to decompose already at 120°C probably releasing formaldehyde from  $N$ -hydroxymethyl groups (Fig. 9a). As temperature increases, the parabanic acid ring starts to decompose, as well. The liquid product of reaction of 1 mole of parabanic acid with four moles of formaldehyde starts to decompose as early as at 60°C, but the highest decomposition rate is observed again at 120°C (Fig. 9b). From TG and DTA curves it follows that formaldehyde gets liberated easier from  $O$ -hydroxymethyl groups than from  $N$ -hydroxymethyl ones and probably yields  $N,N'$ -bis(hydroxymethyl) parabanate, which decomposes further at 120°C.

#### Attempts at Further Polymerization

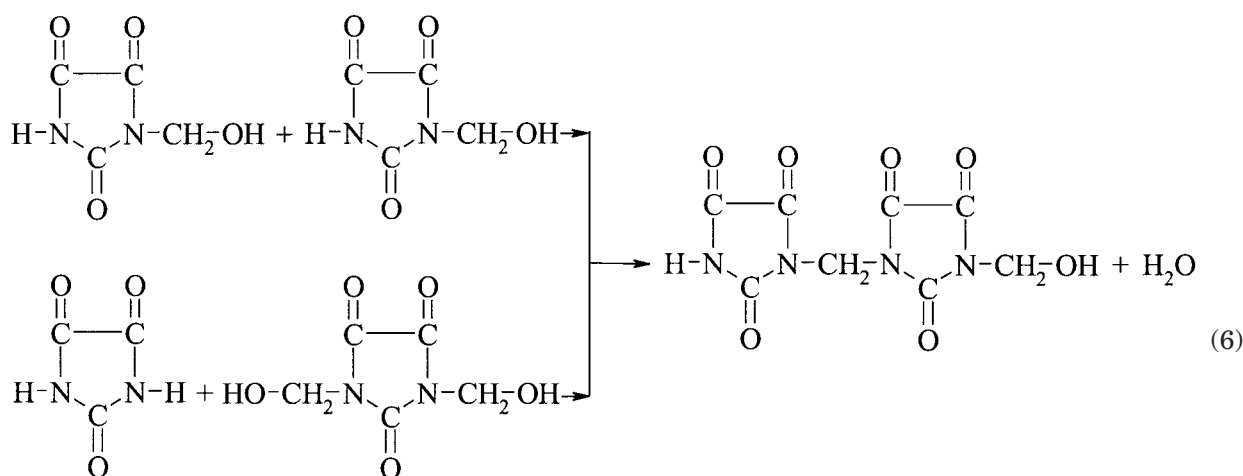
The next step of the study was to polymerize  $N,N'$ -bis(hydroxymethyl)parabanate in either an acidic or a basic solution. The reaction was carried out at 80°C by introducing concentrated sulfuric acid dropwise to a solution of  $N,N'$ -bis(hydroxymethyl)parabanate kept for 2 h in formalin at this temperature (Table II, run 1). An attempt was also made to introduce sulfuric acid after 20 min (Table II, run 2). The main difference between the two attempts above was that, in the first, diluted formalin was used (16.9 wt %), whereas regular formalin was applied in the second attempt. By measuring the acid number and formaldehyde content, it was found that the main product was still  $N,N'$ -bis(hydroxymethyl)parabanate, but some condensation took place. The combining of  $N,N'$ -bis(hydroxymethyl)parabanate with aqueous sodium hydroxide leads to the formation of disodium parabanate. The instability of  $N$ -hydroxymethyl-substituted imides was pointed out by Sidney and Pierce.<sup>15</sup> IR spectra provided evidence for the degradation of  $N,N'$ -bis(hydroxymethyl)parabanate. As the reaction progresses, the stretching vibrations of  $\text{—OH}$  groups in the range 3300–3500  $\text{cm}^{-1}$  as well as deformational ones at 1070  $\text{cm}^{-1}$  vanish, the carbonyl group band moves from 1745  $\text{cm}^{-1}$  in

**Figure 9** Thermal analysis (a) of  $N,N'$ -bis(hydroxymethyl)parabanate and (b) of the product of reaction of parabanic acid with formaldehyde at molar ratio 1:4.

the spectrum of parabanic acid to  $1660\text{ cm}^{-1}$  in the product spectrum, and a small band appears at  $1534\text{ cm}^{-1}$  ( $-\text{C}=\text{N}-$  from the bonds), confirming the possibility of partial enolization of the product disodium parabanate or a semi-product.

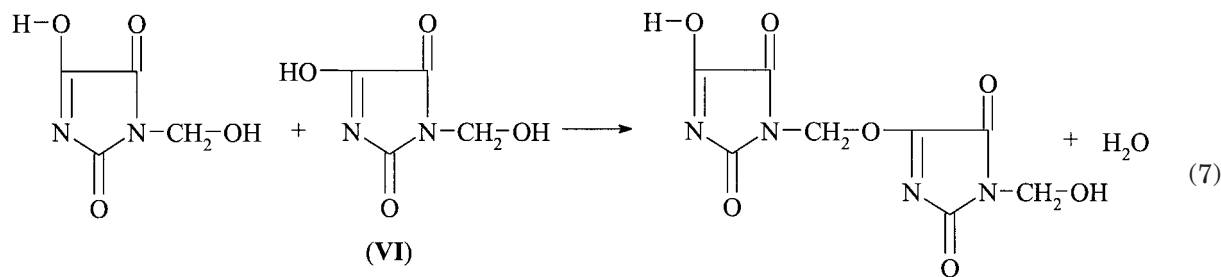
Attempts have also been made to polymerize the product of the reaction of parabanic acid with formaldehyde that was obtained at the molar ratio 1:1 in the presence of the triethylamine catalyst (Table II, run 3). Substances were obtained in these attempts of IR spectra identical with that of *N,N'*-bis(hydroxymethyl)parabanate. For the reaction carried out at room temperature in the absence of triethylamine in dilute formalin (1.45 wt % of  $\text{CH}_2\text{O}$ ) (Table II, run 4), a reduction in the intensity of the deformational vibrations of  $-\text{C}-\text{OH}$  was observed in the IR spectrum. This may suggest that some condensation involving

*N*-hydroxymethyl groups does take place. At elevated temperature ( $50-90^\circ\text{C}$ , Table II, run 5), the intensity of the band further decreases and bands at  $1500-1660\text{ cm}^{-1}$  appear instead due to the presence of  $-\text{C}=\text{N}-$  in the product. The results of the formaldehyde determination (Table II) clearly confirm the contribution of hydroxymethyl groups in the condensation. Since, as shown above, *N,N'*-bis(hydroxymethyl)parabanate does not undergo condensation in an acidic medium to yield  $-\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-\text{N}-$  bridges, one might expect that the condensation of parabanic acid with its hydroxymethyl derivatives takes place through the formation of methylene bridges  $-\text{N}-\text{CH}_2-\text{N}-$ . They are formed in the self-condensation of *N*-hydroxymethyl hydroparabanate (III) or in the condensation of *N,N'*-bis(hydroxymethyl)parabanate with parabanic acid. Both reactions lead to the same product:



Since a signal at 4.65 ppm due to methylene groups of the form  $-\text{O}-\text{CH}_2-$  appears in the  $^1\text{H-NMR}$  spectra of these products, one cannot

exclude the condensation of the semienolic form of *N*-hydroxymethyl parabanate (VI):



When multiplied, these reactions lead to the formation of oligomers insoluble in water and organic

solvents, except of hot dimethyl sulfoxide. These oligomers have been found to decompose at  $212-240^\circ\text{C}$ .

**Table III** Content of Formaldehyde in Products of Reaction of Successive Moles of Ethylene Oxide (EO) with the Hydroxymethyl Derivative of Parabanic Acid (PA) Obtained at Molar Ratio of the Latter to Formaldehyde Equal to 1 : 4

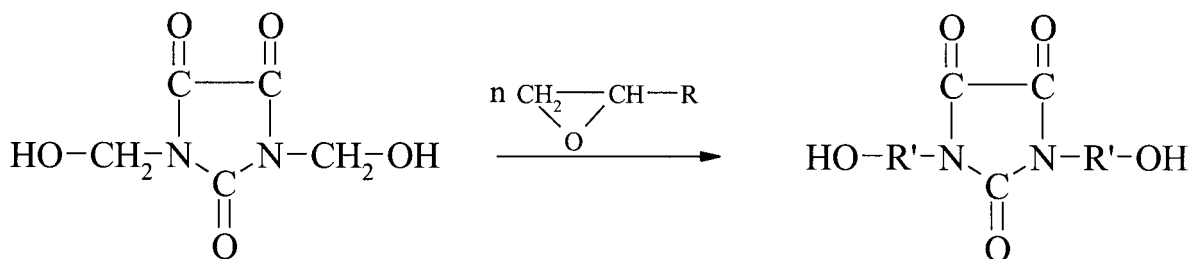
Run	PA Hydroxymethyl Derivative : EO Molar Ratio	Wt % of CH <sub>2</sub> O		Moles of Labile CH <sub>2</sub> O
		Calculated	Found	
1	1 : 1	43.2	43.2	4.0
2	1 : 2	37.3	37.2	4.0
3	1 : 3	32.8	31.8	3.9
4	1 : 4	29.3	27.9	3.8
5	1 : 6	24.1	21.9	3.6
6	1 : 8	20.5	3.6	0.7
7	1 : 10	17.8	3.1	0.7

In concluding, one may state that polycondensation leading to the formation of polymers (oligomers) containing parabanic acid rings in their structure takes place at the molar ratio of parabanic acid to formaldehyde of 1:1 or after combining equimolar amounts of parabanic acid and *N,N'*-bis(hydroxymethyl)parabanate. The polymerization takes place spontaneously without catalysts with a possible autocatalytic function of parabanic acid protons. The resulting polymer is composed of parabanic acid rings linked through —N—CH<sub>2</sub>—N— or —N—CH<sub>2</sub>—O— bridges.

Hence, one should expect a partial enolization of parabanic acid to play some role in the polymerization.

#### Prospects of Hydroxymethyl Derivatives of Parabanic Acid in Polymer Chemistry

Both parabanic acid and its hydroxymethyl derivatives can be further oxyalkylated by, say, reacting them with oxiranes (ethylene oxide or propylene oxide) to obtain bifunctional oligoetherols containing a parabanic acid ring:



with —R standing for —CH<sub>3</sub> or —H, and R' is an oxyalkylene group of the form —CH<sub>2</sub>O—R''—OH or —R''—OCH<sub>2</sub>OH, where R''— is a polyoxyethylene or polyoxypropylene chain.

No solvent is required in this reaction, since both parabanic acid and its hydroxymethyl derivatives dissolve in oxiranes. (The solubility of parabanic acid and *N,N'*-bis(hydroxymethyl)parabanate in 100 g of propylene oxide is 1.67 and 1.21 g, respectively.) By using an excess of oxirane with respect to parabanic acid or its derivative, one obtains oligoetherols with different lengths of the polyoxyalkylene chain R'. Even better possibilities offer the product of the reac-

tion of 1 mol of parabanic acid with 4 mol of formaldehyde. It has the form of a viscous liquid and mixes with oxiranes in all proportions. As preliminary experiments suggest, in the product of its oxyethylation with 4 mol of ethylene oxide, the latter does not block the formaldehyde that is initially present in the form of —N—(CH<sub>2</sub>O)<sub>2</sub>H groups (Table III), but makes it move to the end of the polyoxyalkylene chain, similarly as in hydroxymethyl derivatives of isocyanuric acid or melamine.<sup>14,16</sup> Formaldehyde becomes blocked only when at least an 8-fold molar excess of oxirane is used. Hence, the advantage of the derivative being fully miscible with oxirane is compen-

sated by the disadvantage of the need to use a large excess of oxirane to obtain stable oligoetherols. The oligoetherols can be used in the preparation of polyesters and polyurethanes of a thermal stability improved by the presence of the parabanic acid ring. Details on the reactions of oxiranes with hydroxymethyl derivatives of parabanic acid and with the acid itself will be described in forthcoming papers.

## REFERENCES

1. Piskala, A.; Gut, J. *Collect Czech Chem Commun* 1962, 27, 1562.
2. Dean, J. *Lange's Handbook*; McGraw-Hill: New York, 1972; pp 7-460.
3. Hladik, V. *Int Polarogr Congr Prague Part I* 1951, 680-687; *Chem Abstr* 1952, 10958.
4. Brojer, Z.; Hertz, Z.; Penczek, P. *Epoxy Resins*; WNT: Warsaw, 1972; p 74 (in Polish).
5. Porret, D. *Makromol Chem* 1967, 108, 73; *Chem Abstr* 1967, 67, 108599z.
6. Patton, T. L. U.S. Patent 3 661 859, Sept. 5, 1972.
7. Patton, T. L. U.S. Patent 3 684 773, Aug. 15, 1972.
8. Scortanu, E.; Nicolaescu, I.; Caraculacu, A. *Eur Polym J* 1998, 34, 1265.
9. Oda, R.; Baba, R. *Kogyo Kagaku Zasshi* 1961, 64, 741.
10. Cassidy, P.; Fawcett, W.; Thomas, R. *J Appl Polym Sci* 1981, 26, 3819.
11. Murray, J. *Org Synth* 1967, 37, 61.
12. Kastierina, T.; Kalinina, L. *Chemical Analysis of Plastics*; WNT: Warsaw, 1965; p 141 (in Polish).
13. Duliban, J.; Galina, H.; Lubczak, J. *J Appl Spectrosc* 1996, 50, 528.
14. Kucharski, M.; Lubczak, J.; Rokaszewski, E. *Chem Stosowana* 1983, 27, 65.
15. Sidney, L.; Pierce, A. *J Org. Chem* 1972, 37, 3.
16. Lubczak, J. *Polimery (Warsaw)* 1995, 40, 509.