MOLECULAR STRUCTURE OF A CYCLIC DIMERIC MODEL OF POLY(6-HEXANELACTAM)

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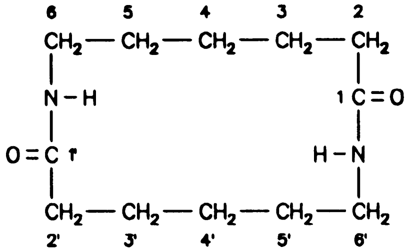
Received April 6, 1993
Accepted April 30, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Two crystalline forms of the cyclic dimer of 6-hexanelactam were studied by DSC, Raman, IR, NMR and computational methods. It was found that the high-temperature modification contains the energetically most favoured conformational structure, the low temperature modification contains the energetically less favoured conformation stabilized by stronger hydrogen bonds.

Cyclic oligomers of 6-hexanelactam are characteristic products formed in the polymerization of 6-hexanelactam, in addition to open chain macromolecules. The most important of them is the cyclic dimer of 6-hexanelactam, 1,8-diaza-2,9-dioxocyclotetradecane (*I*).



I

This cyclic amide was first mentioned by Hoshino[1,2] as a crystalline compound with m.p. 341 °C. Further, two modifications of this compound were distinguished by Hermans[3]. The low-temperature modification crystallizes from water or ethanol in the form of rectangular plates. The transformation into the high-temperature modification can be effected by heating these crystals in vacuo (with exclusion of moisture) at 250 °C. Very fine needles are formed on the cold parts of the evacuated sealed tube. This modification of the cyclic dimer is not stable below 250 °C and, at room temperature, it transforms slowly into the low-temperature form. After wetting with water or alcohol the needles undergo a rapid transformation into the low-temperature modification.

So far only the structure of the stable form of the cyclic dimer has been investigated. IR spectroscopic studies[4] showed, in agreement with the assumption made by Dale[5], that two parallel methylene chains are linked by two planar amide groups in the stable conformation. The stable conformation of the 14-membered ring, which consists of two pairs of planar elements related by a symmetry centre, was also proposed on the basis of an X-ray crystallographic study[6]. No intramolecular hydrogen bonds were proved.

As the molecular structure of the two forms of the cyclic dimer is interesting not only as such but can reveal valuable hints about the forces acting in the folding of polyamide chains, we present here a detailed study of both forms using DSC, spectroscopic and theoretical methods.

EXPERIMENTAL

Sample Preparation

1,8-Diaza-2,9-dioxocyclotetradecane (*I*) was isolated[7] from the concentrated aqueous exctracts of the polyamide rayon production (Chemlon Works, Humenné, The Slovak Republic), three times recrystallized from methanol and dried at 20 °C/7 Pa. The separated product was tested by mass spectrometry. The purity of *I* proved by HPLC is 99.9%. The recrystallized sample of *I* was designated as A. A part of this sample was heated in an evacuated and sealed glass ampoule at 260 °C for 1 h and designated as B. According to HPLC analysis, A and B are chemically identical compounds.

DSC

DSC measurements were performed using a Du Pont 2000 Thermal Analysis-DSC cell instrument in the temperature range 20 – 360 °C with a constant heating rate of 10 °C/min under nitrogen atmosphere.

Raman Spectra

Raman spectra were obtained with a Coderg LRDH 800 spectrometer. The spectra were excited by the 514.5 nm line of a Spectra Physics Stabilite 2017 argon laser. Solid samples of the A and B forms of *I* were measured at room temperature in glass tubes under vacuum. Due to the low signal-to-noise ratio only the 1 700 – 1 400 cm^{-1} region of the spectra in hexafluoroisopropyl alcohol (HFIP) solutions (0.1 g/ml) could be measured.

IR Spectra

The KBr pellet technique was not used as in grinding and pressing with KBr the B structure tends to transform into the original, more stable A. Instead, the diffusion reflection infrared spectroscopy

(DRIFT) was used. The samples were measured as neat powders or were only gently mixed with the ground KBr so that practically no structural transformation could occur.

To investigate the transformation of the A form during heating, the sample in the KBr pellet was put into a Perkin–Elmer heating infrared cell and the spectra were followed in the range 30 – 350 °C.

The spectra of *I* in HFIP (0.05 – 0.1 g/ml) were measured in the KRS-5 and AgBr cells. The temperature dependence of the solution was measured in the range from –4 to +54 °C using a temperature-controlling device.

IR spectra were measured using a FT-IR spectrometer Bruker 88 and a grating spectrometer Perkin–Elmer 580B connected on-line with a Tracor TN 4000 computer system.

NMR Spectra

NMR spectra in CF_3COOD (TFA) (0.05 g/ml) and HFIP (0.1 g/ml) solutions were measured at ambient temperature using a Varian Unity-500 spectrometer operating at 499.8 MHz for ^1H NMR and 125.7 MHz for ^{13}C NMR. Hexamethyldisiloxane (HMDS) was used as an internal standard in °C NMR (δ = 2.0 ppm).

^{13}C CP/MAS NMR spectra of solid samples were measured with a Bruker MSL 200 spectrometer at 50.3 MHz at ambient temperature. Chemical shifts were referred to the carbonyl band of glycine (δ = 176.0 ppm) by sample replacement.

RESULTS AND DISCUSSION

DSC

As follows from the DSC thermograms of the A and B forms of *I* (Fig. 1), their thermal behaviour is not identical. Both thermograms show endotherms centred at 344.6 °C corresponding to the published melting point of the cyclic dimer of 6-hexanelactam (ΔH = 49.3 kJ/mol). They differ in the endotherm centred at 244.2 °C (ΔH = 13.6 kJ/mol) which appears only with the A form. With regard to the chemical identity

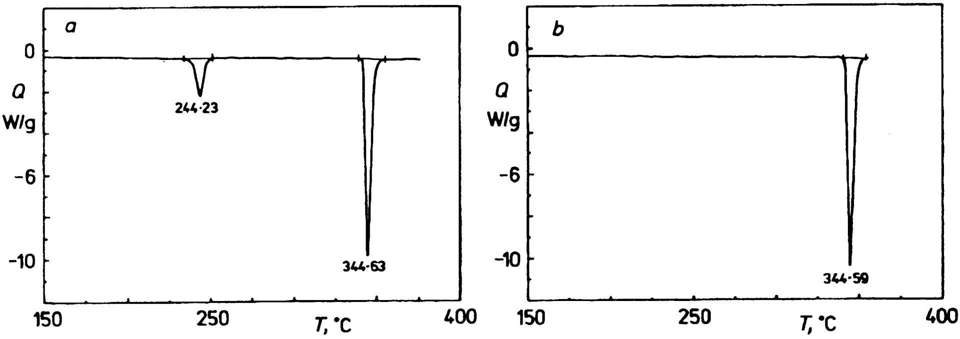


FIG. 1
DSC of *I*: *a* form A, *b* form B

of both samples, this finding gives an indirect evidence of a significant change in the structure of the cyclic dimer molecule. Repeated DSC measurements of sample B stored in a closed ampoule under air at room temperature for one month showed the typical endotherm of the A form centred ~ 100 °C below the melting point. This clearly indicates that in the presence of air, the B form is not stable. However, when B is stored under argon for one month, its DSC thermogram is identical with that of the freshly prepared form B.

Direct microscopic observations during the heating of sample A showed a change in the crystal structure near 240 °C (heating rate about 10 °C/min) – the original rectangular plates were transformed into well developed needles.

The observed phenomena have stimulated the following detailed study of the structure of the cyclic dimer of 6-hexanelactam by spectroscopic methods as the needle crystals of form B, due to their dimensions, were unsuitable for X-ray diffraction study.

Calculations

The permitted conformational structures of the isolated molecule of *I* were studied by the molecular mechanics method (MM2 force field[8]) and by the semiempirical AM1 molecular orbital method[9]. All the structures were calculated using the full geometry optimization procedure. The stable forms of *I* shown in Fig. 2 were obtained by a detailed inspection of the potential energy surface. Geometry optimizations were run using different starting geometries both with parallel and with antiparallel amide groups. The methylene groups of the $-(CH_2)_5-$ sequences form all-trans structures in

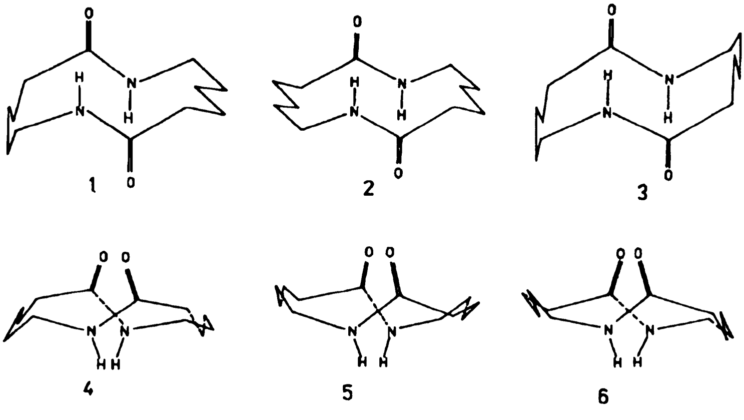


FIG. 2
Calculated stable structures of *I*

all the found stable forms of *I*. The calculated energies of the stable forms relative to the global energy minimum obtained by the MM2 and AM1 methods are given in Table I. According to the results of both methods, the conformational form 1 is energetically most favoured. The conformational form 2 present in sample A according to the X-ray structure determination[6] is less stable by 1.3 kJ/mol (MM2) or 5.0 kJ/mol (AM1). The conformational forms with parallel amide groups (4, 5 and 6) are predicted to be by some 4 kJ/mol higher in energy in comparison with the corresponding antiparallel structures.

Raman Spectra

Raman spectra of the A and B forms of *I* are shown in Fig. 3. The two spectra differ both in the band wavenumbers and in the band intensities. The bands at 1 320 and

TABLE I
Relative energies (kJ/mol) of the stable conformational structures of *I* calculated by the MM2 and AM1 methods

Structure[a]	MM2	AM1
1	0.0	0.0
2	1.3	5.0
3	3.8	1.0
4	6.3	4.1
5	8.5	8.1
6	8.9	9.7

[a] See Fig. 2.

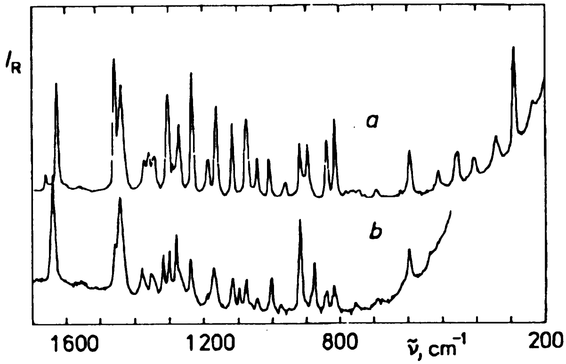


FIG. 3
Raman spectra of *I*: *a* form A, *b* form B

1 098 cm^{-1} appear only in the spectrum of form B; the band at 895 cm^{-1} in the spectrum of form A is shifted to 875 cm^{-1} in the spectrum of form B. In the CH_2 wagging region, bands at 1 371, 1 359 and 1 343 cm^{-1} appear in form A, while bands at 1 378 and 1 350 cm appear in form B. In the amide I region, a doublet at 1 660 and 1 628 cm^{-1} can be observed in the spectrum of sample A while only one band at 1 640 cm^{-1} appears in the spectrum of sample B.

The observed splitting of the amide I vibration in the spectrum of form A and the differences between the amide I bands in the spectra of forms A and B can be explained by the transition dipole coupling interactions of the amide groups in the ordered crystalline structures[10]. However, other differences between the two spectra described above indicate the presence of different conformational structures of *I* in forms A and B. The measured samples A and B contain pure structural forms since the characteristic Raman bands of one sample are not detected in the spectrum of the other.

In the spectrum of the solution of *I* in HFIP (Fig. 4), the amide I mode (doublet at 1 648 and 1 620 cm^{-1}) is complicated by hydrogen bonds of *I* and solvent molecules. A comparison of the band intensities in the CH_2 bending region (1 430 – 1 460 cm^{-1}) of the spectra of *I* in solution and in the solid state indicates that the predominant conformational structure is similar to that of B.

IR Spectra

The DRIFT spectra of the A and B samples of *I* in the solid state are shown in Fig. 5. The spectra of both forms exhibit bands characteristic of the N–H stretching vibrations (at 3 266 cm^{-1} and 3 300 cm^{-1} in A and B, respectively), of the amide I vibration (1 636 cm^{-1} for A and 1 639 cm^{-1} for B) and of the amide II vibration (1 560 cm^{-1} for A and 1 555 cm^{-1} for B). The bands at 2 979, 845, 766, 429 and 405 cm^{-1} can be found only in the

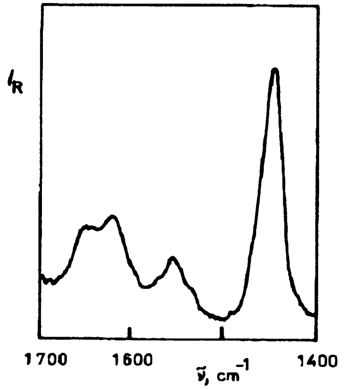


FIG. 4
Raman spectra of *I* in HFIP solution (0.1 g/ml)

spectrum of form A and the bands at 677, 610, 487 and 385 cm^{-1} only in the spectrum of form B. There are some other bands by means of which both forms can be discerned. The intensity of such bands is considerably greater in one of the forms (e.g., the band at 590 cm^{-1} in A) or their wavenumbers differ slightly (993 cm^{-1} in A and 998 cm^{-1} in B).

The temperature changes of the spectrum of A in a KBr pellet can be seen in Fig. 6. The wavenumber of the N–H stretching vibration considerably increases with increasing temperature, reflecting the weakening of hydrogen bonds. At 120 °C, the wavenumber shift is 10 cm^{-1} and in the spectrum of the melt (350 °C), the shift reaches ~50 cm^{-1}. Starting from ~250 °C the absorption at 610 cm^{-1} begins to increase with increasing temperature, at the expense of the 590 cm^{-1} band; this reflects an increase in the content of structure B. The increase in the intensity ratio A_{610}/A_{590} becomes more pronounced after cooling the sample to room temperature. By grinding and pressing the samples with KBr, the intensity ratio A_{610}/A_{590} also decreases; the A crystal structure is restored.

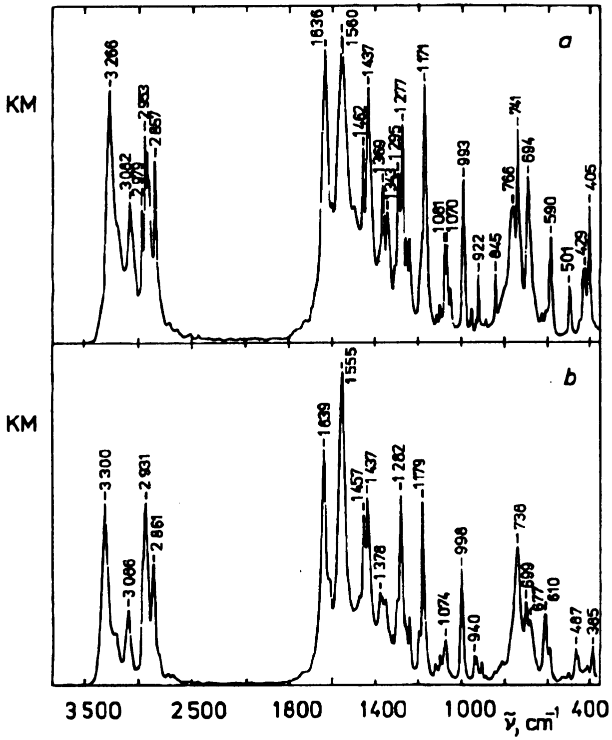


FIG. 5

Diffusion reflection IR spectra of *I* (KBr, 5%): *a* form A, *b* form B (KM, Kubelka–Munk function)

In the spectrum of the melt at 350 °C (Fig. 7), the N–H stretching, amide I and amide II bands are slightly shifted (to ~3 320, 1 645 and 1 544 cm^{-1}, respectively). Otherwise, we can find here the bands corresponding to both forms, A and B.

In the spectra of the HFIP solution of *I*, the bands corresponding to the N–H stretching and amide I vibrations are strongly shifted to 3 138 and 1 613 cm^{-1}, respectively. The spectra are shown in Fig. 8, where we can also see the temperature dependence of the spectra. From the figure it follows that with increasing temperature, the intensity ratio A_{610}/A_{590} and the wavenumber of the centre of the band near 1 000 cm^{-1} decrease, which corresponds to the decrease in the content of the form resembling structure B (compare Fig. 5). The wavenumber of the N–H stretching band near 3 200 cm^{-1} increases and the wavenumber of the amide II band decreases with increasing temperature, which corresponds to a weakening of hydrogen bonds.

NMR Spectra

In all the ^{13}C NMR spectra of *I* in TFA and HFIP solutions, six carbon resonances were found; the band at 41.2 ppm in the HFIP solution is assigned to the carbon of the NH–CH$_2$ group in analogy with other cyclic amide compounds[11,12]. Using a combination of COSY and HETCOR spectra[13] all the ^{13}C bands were assigned. The full assignment is given in Table II. It can be seen that the ^{13}C chemical shifts of *I* depend strongly on the solvent similarly to other reported amide compounds[11,12].

In ^{1}H NMR spectra of *I* in TFA and HFIP solutions, five multiplets corresponding to the CH$_2$ groups were found, well resolved in HFIP solution. However, it is not possible to distinguish axial and equatorial positions. This indicates that fast (in the NMR time scale) exchanges between different conformational structures of *I* occur in the solutions.

^{13}C CP/MAS NMR spectra of the solid A and B are shown in Fig. 9. The spectrum of A contains only five strong bands with the band at 26.8 ppm having double intensity

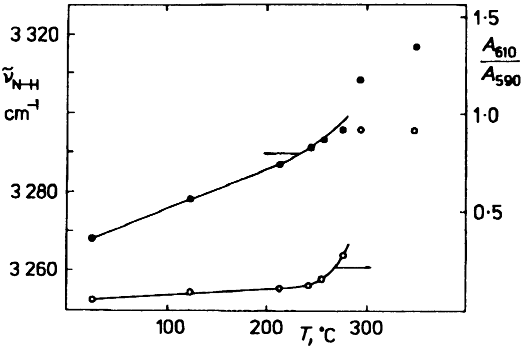


Fig. 6

Influence of the temperature on the IR spectrum of the A form of *I* (KBr): ● wavenumber of the maximum of N–H stretching band, ○ intensity ratio of the bands at 610 and 590 cm^{-1}. The curves are not drawn in the region near the melting point relative to the other CH_2 bands. Using the solution spectra of *I* all the bands could be assigned (Table II). The fact that in the ^{13}C CP/MAS NMR spectrum of form A only five bands were detected (one with double intensity) indicates that molecules of *I* in form A have a structure with the primed and unprimed carbon atoms in equivalent positions. This is in agreement with its crystalline structure obtained by X-ray analysis[6].

The ^{13}C CP/MAS NMR spectrum of B differs from that of A by the number of bands (Fig. 9). The spectrum of form B exhibits two bands corresponding to the carbonyl carbon: one of the bands has the same position as in the spectrum of A (174.7 ppm) and the other is shifted by 3 ppm to the higher field (171.7 ppm). A new band at 34.3 ppm appears and the intensity of the band at 37.1 ppm is decreased. This indicates that the positions of bands corresponding to the C-1 and C-1′ carbons and to the C-2 and C-2′ carbons differ. This can be caused by an asymmetric molecular structure of B or by intermolecular forces in the lattice. The fact known from the IR spectra, that the two structures of *I* are present in the liquid state, together with the band positions in two different solutions and in the solid state (Table II) permit the conclusion that the non-

TABLE II
^{13}C NMR chemical shifts (δ, ppm) of *I*

Measured as	C-1, C-1′	C-2, C-2′	C-3, C-3′	C-4, C-4′	C-5, C-5′	C-6, C-6′
TFA solution	184.4	38.6	29.2	29.5	31.6	46.3
HFIP solution	180.1	37.9	26.5	26.9	29.6	41.2
Solid form A	174.7	36.4	26.8	26.8	30.9	39.1
Solid form B	174.9	37.1	25.8	25.8	30.7	39.4
	171.7	34.3				

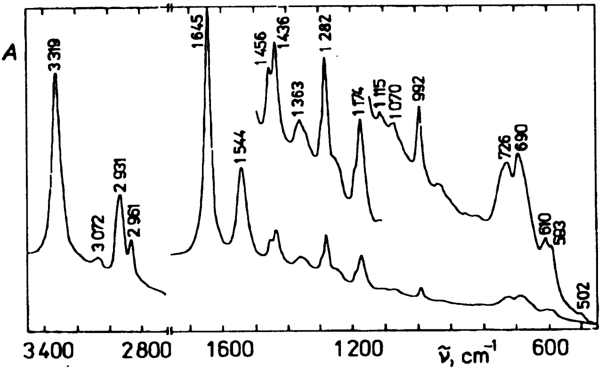


FIG. 7
IR spectrum of the melt of *I* at 350 °C (KBr)

equivalency of C-1, C-1′ and C-2, C-2′ carbons is caused by the asymmetry of the conformational structure.

CONCLUSIONS

Summarizing the NMR, IR, Raman and computational (MM2 and AM1) investigations of the conformational structure of *I* in both crystalline forms and in solution, we can conclude that in the more stable form A, the conformational structure 2 (Fig. 2) is present, while the less stable form B, has the conformational structure 1 (Fig. 2). For the isolated molecule of *I*, the structure 1 is energetically the most favoured (Table I). This is fully supported by the IR spectra of the solutions of *I* showing that the conformational structure of *I* present in the crystalline form B is its most favoured structure in solution. In the solid state, the higher stability of the crystalline form A relative to the B form is caused by stronger intermolecular hydrogen bonds in A. This is documented in the IR spectra of A by the 34 cm^{-1} shift of the N–H stretching band to lower wavenumbers. The fact that the more stable form A is formed by the less favoured conformational structure of *I* is in agreement with the IR spectra of the solid samples measured at different temperatures. On heating, the hydrogen bonds are loosened (see the N–H stretching wavenumber shift with temperature, Fig. 6). The conformational structure 1 of *I* begins to appear some 100 °C below the melting point, when the hydrogen bonds have been sufficiently weakened, and its content increases with increasing temperature.

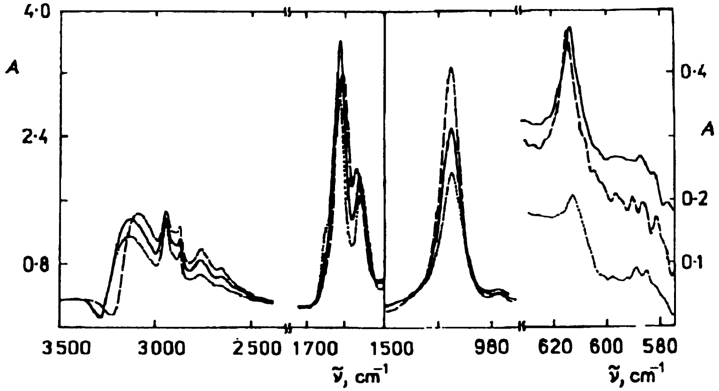


FIG. 8

IR spectra of *I* in HFIP (0.05 g/ml, 0.1 mm AgCl cell) at temperature *T* (°C): −2 (- - -), 25 (——), 54 (· · · ·)

The transition of the form B into the form A is promoted by traces of moisture. This follows from the comparatively rapid transition in air compared with the stability of form B in vacuum or in dry argon.

In the IR spectra of the solutions of *I*, no new band appeared which could be assigned to other possible conformational structures predicted by the MM2 and AM1 calculations (Table I). This can be explained by the low contents of these conformations, in agreement with the calculated relative energies (Table I). Another explanation could be that in structures 3, 4, 5 and 6, the local conformations of the CO–NH–$(CH_2)_5$ groups are similar to those in structures 1 and 2, and hence their IR spectra are not much different.

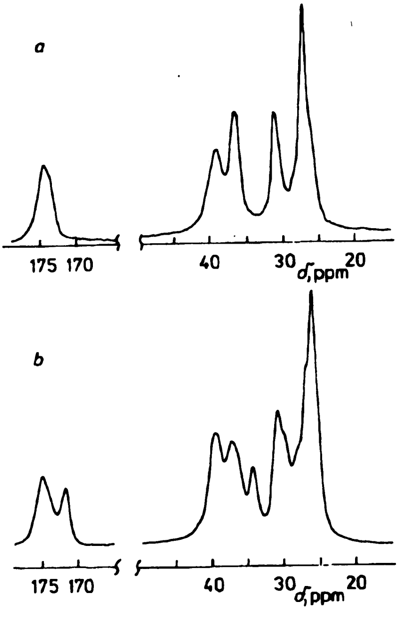


FIG. 9
^{13}C CP/MAS NMR spectra of *I*: *a* form A, *b* form B

REFERENCES

1. Hoshino K.: Bull. Chem. Soc. Jpn. *19*, 171 (1944).
2. Hoshino K., Abe Y.: J. Chem. Soc. Jpn. *64*, 628 (1943); *65*, 419 (1944); *67*, 99 (1946).
3. Hermans P. H.: Rec. Trav. Chim. Pays-Bas *72*, 798 (1953).
4. Heidemann G., Nettelbeck H. J.: Faserforsch. Textiltech. *18*, 183 (1967).
5. Dale J.: J. Chem. Soc. *1963*, 93.
6. Northolt M. G., Alexander L. E.: Acta Crystallogr., B *27*, 523 (1971).
7. Zahn H., Spoor H.: Chem. Ber. *89*, 1296 (1956).

8. Allinger N. L.: J. Am. Chem. Soc. *99*, 8127 (1977).
9. Dewar M. J. S., Zoebisch E. G., Healy E. F., Stewart J. J. P.: J. Am. Chem. Soc. *107*, 3902 (1985).
10. Krimm S.: Biopolymers *22*, 217 (1983).
11. Williamson K. L., Roberts J. D.: J. Am. Chem. Soc. *98*, 5082 (1976).
12. Winkler T., Leutert T.: Helv. Chim. Acta *65*, 1760 (1982).
13. Derome A. E.: *Modern NMR Techniques for Chemistry Research*. Pergamon Press, Oxford 1987.

Traslated by D. Doskočilová.