Helical configuration of poly(tert-butyliminomethylene).
Complete resolution and maximum optical rotation

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Abstract. By repeated chromatography over optically active poly(see-butyliminomethylene) on glass beads complete resolution of poly(tert-butyliminomethylene) was obtained. The specific rotation increases with molecular weight up to \([\alpha]_s^{28} = 56 \pm 2^\circ\) at approximately 20 repeating units.

Introduction

Poly(tert-butyliminomethylene), I, is obtained by polymerisation of tert-butyl isocyanide with nickel chloride as catalyst.

\[
\begin{align*}
\alpha & \quad \beta' \quad \gamma' \\
\gamma & \quad \beta \quad \alpha', \gamma'
\end{align*}
\]

\[
\text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C}
\]

\[
\alpha \quad \beta \quad \alpha', \beta' \quad \gamma
\]

\[
\text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C}
\]

\[
\alpha \quad \beta \quad \alpha', \beta' \quad \gamma
\]

Fig. 4. Nomenclature used in the description of acetal groups and Newman projections showing the possible conformations.

\(\sigma^*\)-bonding interaction between the oxygen lone-pair (e.g. atom Oβ) in Fig. 4 with the anti-bonding orbital of the adjacent bond carrying the most electronegative group (here Cα—Oβ). The stereochemistry of the interaction favours situation I (Fig. 4) over II, thus leading to a synclinal-synclinal conformation of the alkoxy groups. The experimental torsion angles in the four C—O—C—O chains (Table VI) are on the average 55°. Also, the increasing electron density in the Cz—Oβ region is responsible for the observed shortening of the “central” C—O bonds (see above).

Coinciding with this shortening there is often a lengthening of the “peripheral” Cγ—Oβ bonds. Despite ample experimental evidence (e.g. in carbohydrates, sulfites and phosphates) the phenomenon seems to have gone unnoticed.

Finally, the central C and O atoms, under the anomic influence, tend to a more sp²-like hybridization causing their valency angles to enlarge to values of 115° ± 3°. This view is corroborated by the results of Gorenstein et al., which showed a coupling of the RO—X—OR (X = C or P) bond angle to a rotation about the O—X bond, the larger valency angle corresponding with the smaller torsion.

Experimental

Details of the formation 2–4 will be described elsewhere. Crystals of 6-(bromomethyl)-1,2,4-trichloro-3-ethoxy-3,7,7-trimethoxybicyclo[2.2.1]heptane (henceforth NORB) were obtained by slow evaporation from hexane. The crystallographic unit cell as well as the relevant information about the data collection and applied structure determination methods are summarized in Table I. The final values of the parameters of NORB are listed in Tables II and III (see fig. 1a for the numbering of the atoms).

Although the final difference Fourier showed maxima up to 1.5 e/Å³, it did not yield refinable hydrogen positions, neither was it possible to refine all non-hydrogen atoms anisotropically to physically acceptable values for the temperature factors. These difficulties we encountered during the analysis may well be due to the presence of disorder, which is not an uncommon feature with norbornanes.

Acknowledgement

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4 H. J. Geise, C. Altona and C. Romers, Tetrahedron Let. 1383 (1967);
5 D. G. Gorenstein and D. Kar, J. Amer. Chem. Soc. 99, 672 (1977);
6 J. van Bree and M. J. O. Anteunis, unpublished results.
Results and discussion

The earlier resolution of 1 was performed by chromatography on a column of poly(sec-butyliminomethylene) prepared from optically active sec-butyl isocyanide. However, the packing of the column was troublesome and the elution slow. The chromatography process has now been very much improved by applying the poly(sec-butyliminomethylene) as a coating on glass beads. The monomer (S)-(+) -sec-butyl isocyanide was polymerised in the presence of nickel chloride treated porous beads. It was very easy to pack a column with these beads; it showed excellent flow properties and it could be used an unlimited number of times.

Samples of approximately 300 mg of racemic 1 (M₁₈₀ = 860) were dissolved in 0.5–1 ml of chloroform, introduced into the column and eluted with the same solvent. This process was repeated with additional portions of racemic 1. Correlating fractions were dissolved in 0.5-1 ml of chloroform, introduced into a column of poly(sec-butyliminomethylene) as a coating on glass beads. The monomer Mn = 860 was chromatographed on a Sephadex LH 20 column which separates into molecular weight fractions. Three successive fractions were collected. The first and second fractions, which will contain the higher molecular weights, have [α]₉₀°_293 = +56° (estimated error 2°), while the third fraction (±20 weight %) has [α]₉₀°_293 = +26°. Molecular weight measurements reveal that the specific rotation increases with molecular weight until the maximum of [α]₉₀°_293 = +56° is reached at a number average molecular weight of approximately 1900 or at a chain length in the order of 20 repeating units. The corresponding molar rotation per repeating unit (CH₃(CH₂)₃C=N-C≡C [M]₂⁰°₉₀ = 46°. In SI units [CHCl₃, 293 K, 578 nm] nm = 56° should be αₙ (CHCl₃, 293 K, 578 nm) = 9.8 x 10⁻³ m²kg⁻¹ and [M] = 46° should be αₙ = 0.84 x 10⁻³ m²mol⁻¹. The rotation does not decrease when the compound is kept in solution at room temperature for months.

We also observed an increase in [α] with increasing molecular weight for poly((S)-α-phenylethyliminomethylene); a sample of M₁₈₀ = 1830 had [α]₂⁰°₉₀ of -250° while samples of M₁₈₀ = 14,000 and 66,000 had [α]₂⁰°₉₀ of -350° (see also ref. 7). The corresponding low molecular weight model, CH₃(CH₂)₃C-N=C(CH₃)₃ has αₙ [HCl, 293 K] = -90° (cf. ref. 12). These observations of increasing [α] with increasing molecular weight are in line with calculations which predict that the optical rotation per repeating unit in any helical polymer increases with molecular weight until a constant value is obtained at 16-20 units.

We tested whether the column would also be suitable for the resolution of low molecular weight compounds. We tried sec-butyl alcohol, sec-butylamine, methyl N-benzoylalaninate and methyl N-benzoylvalinate, but no resolution occurred. Hexahelicene was eluted with chloroform with a very low resolution: ≤0.1% after one run. These results show that specific screw-screw interactions of poly(sec-butyl) with poly(sec-butyliminomethylene) are probably more important than interactions with the chiral side chain of the supporting polymer. It supports our suggestion that the sec-butyl isocyanide has polymerised stereoselectively (cf. Pino et al.14).

In all separations the cumulative weight of the collected fractions is almost equal to the initial sample weight. Moreover, the sum of the products of the weight of each fraction and its specific optical rotation agreed within the experimental error with the product of the weight of the initial sample and its specific optical rotation. These two tests show the reliability of the chromatographic experiments.

In each run the increase in (+)-rotation of the first fraction was higher than the decrease in rotation of the last fraction; the behaviour is not completely symmetrical. The non-symmetrical behaviour is caused by a superposition of separation into molecular weight fractions upon the optical resolution. The molecular weight effect appears from the following observations. The sample with [α]₂⁰°₉₀ = +48° was chromatographed on a Sephadex LH 20 column which separates into molecular weight fractions. Three successive fractions were collected. The first and second fraction, which will contain the higher molecular weights, have [α]₂⁰°₉₀ = +56° (estimated error 2°), while the third fraction (±20 weight %) has [α]₂⁰°₉₀ = +26°. Molecular weight measurements reveal that the specific rotation increases with molecular weight until the maximum of [α]₂⁰°₉₀ = +56° is reached at a number average molecular weight of approximately 1900 or at a chain length in the order of 20 repeating units. The corresponding molar rotation per repeating unit (CH₃(CH₂)₃C=N-C≡C [M]₂⁰°₉₀ = 46°. In SI units [CHCl₃, 293 K, 578 nm] nm = 56° should be αₙ (CHCl₃, 293 K, 578 nm) = 9.8 x 10⁻³ m²kg⁻¹ and [M] = 46° should be αₙ = 0.84 x 10⁻³ m²mol⁻¹. The rotation does not decrease when the compound is kept in solution at room temperature for months.

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11 Calculated from a Mark-Houwink equation, given in Ref. 5.
On the other hand, we also were unable to resolve on our column polymers of isocyanides other than tert-butyl. We tried several of them. Most of them were high molecular weight samples. Their high molecular weight cannot be the only reason of failure because the mixture of poly(tert-aminomethylmethy1ene) with $M_m = 1150$ was resolved. Apparently, the screw-screw interaction is highly specific.

**Experimental part**

Solvents and reagents, unless of analytical grade quality, were purified by standard literature methods\(^{15}\).

**Poly(tert-butylaminomethylene).** N-tert-Butylformamide was made according to a literature method\(^{18}\) and converted into the isocyanide by the method of Casanova\(^{17}\) but at a lower pressure (0.5 mm Hg) than recommended. The yield was 72\% tert-Butyl isocyanide (21.8 g, 263 mmol) was polymerised heterogeneously by anhydride nickel chloride (1.3 g, 10 mmol) without solvent at ambient temperature. After stirring for three days the volatile components were removed under diminished pressure. The resulting solid was dissolved in approximately 100 ml of chloroform, filtered and concentrated to a volume of $\approx 40$ ml. This solution was added dropwise to a vigorously stirred mixture of 500 ml of methanol and 150 ml of water. The flocly yellow precipitate was collected on a glass filter, washed with 25\% aqueous methanol and dried in a vacuum. The yield was 9.5 g (43 \%) of a bright yellow solid. The polymer did not melt on heating to 200°C. IR (KBr): 1630, 1670 cm\(^{-1}\); (S)-enantiomer: $\Delta +40.1°$ (neat); (P)-enantiomer: $\Delta —35.8°$ (neat); (S')-enantiomer: $\Delta —40.9°$ (c, 5, methanol) \[^{15}\]. The corresponding formamide was prepared from the amines by treatment with 10\% excess of ethyl formate\(^{20}\).

Both enantiomers had a melting point of 46-48°C \[^{19}\]. (S)-Monomer. 0.2 Mol % NiCl\(_2\) 6 H\(_2\)O in methanol at 25°C; yield 90\% $\Delta [\alpha] = 0.70$ d/g (toluene, 300°C); $[\alpha]_D = 350°$ (c 1, CHCl\(_3\)). 2 Mol % NiCl\(_2\) 6 H\(_2\)O in methanol at 25°C; yield 90\%; $\Delta [\alpha] = 0.09$ d/g (toluene, 300°C); $[\alpha]_D = 350°$ (c 1-3, CHCl\(_3\)).

**Coating procedure.** To 21 g of porous glass beads (Bio. Rad, Bio-Glass-200, particle size minus 325) was added a solution of 150 mg (0.63 mmol) of NiCl\(_2\) 6 H\(_2\)O in 70 ml of methanol. Subsequently, the mixture was evacuated for a few minutes in order to remove air included in the porous glass beads. The supernatant liquid was decanted and an additional amount of 70 ml of methanol was added to the beads. After standing for 5 min the supernatant liquid was decanted again. After this procedure 7 g (84 mmol) of (S)+(+)sec-butyl isocyanide was added to the beads. The colour of the reaction mixture became red and the polymerisation started after a few minutes, as indicated by a temperature rise. The mixture was shaken until the polymerisation was complete (3 h). Subsequently, the beads were transferred to a glass filter and thoroughly washed with methanol and chloroform. The dry weight of the polymer coated glass beads so obtained was 27 g. In the dry state or in methanol the beads were yellow coloured, but in contact with chloroform their colour was yellow-brown.

For the chromatographic experiments these beads, suspended in chloroform, were transferred into a glass tube, provided with a porous glass bottom. The height of the packing material in the column was 21 cm, the inner diameter of the tube was 1.9 cm. The rate of flow of the eluent during the experiments was regulated within the range of 20–30 ml/h. Fractions were collected and the solvent evaporated under reduced pressure.

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\[^{27}\] L. Thome, Chem. Ber. 36, 582 (1903).

