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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 $[\alpha]_D^{20} = 56 \pm 2^\circ$ at approximately 20 repeating units.

Introduction

Poly(tert-butyliminomethylene), 1, is obtained by polymerisation of tert-butyl isocyanide with nickel chloride as catalyst.

$$n \left(\text{CH}_3\right)_3\text{C}=\text{N}=\text{C} \xrightarrow{\text{NiCl}_2} \left[\left(\text{CH}_3\right)_3\text{C}=\text{N}=\text{C}\right]_n$$

Details of the formation 2-4 will be described elsewhere. Crystals of 6-(bromomethyl)-1,2,4-trichloro-3-ethoxy-3,7,7-trime thoxybicyclo[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/A, 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

Two of us (W.V.D.M. and J.V.B.) thank the Belgian Organisation IWONL for financial support.

6 J. van Bree and M. J. O. Anteunis, unpublished results.
Millich\(^5\) suggested that polymers of isocyanides have helical configurations. In 1974 we partially resolved a solution of 1 in chloroform\(^6\). This resolution proved the polymer to be chiral and thus made the helical configuration highly probable. This configuration is further supported by the optical rotation values of polymers of chiral isocyanides\(^7\) and by the CD spectra of our polymers\(^8,9\). We have now improved the resolution process which enabled us to obtain the maximum rotation of 1\(^10\).

**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\(^6\). 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 (\(\bar{M}_n = 860\)) 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. Corresponding fractions with the higher (+)-rotations were collected. After six runs the corresponding fractions with the higher (+)-rotations were combined and chromatographed again. After six runs the maximum value of \(\left[\alpha\right]_\text{D}^28\) was obtained. The resolution process is illustrated in Table I.

### Table I Chromatographic resolution of poly(tert-butyliminomethylene)\(^a\): packing material poly(\(S\)-sec-butyliminomethylene)\(^b\) on porous glass beads; eluent chloroform.

<table>
<thead>
<tr>
<th>Run (^c)</th>
<th>Fraction</th>
<th>Fraction weight(^d)</th>
<th>(\left[\alpha\right]_\text{D}^28)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1</td>
<td>0.126</td>
<td>+ 7.5°</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>0.130</td>
<td>- 2.0°</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>0.153</td>
<td>- 3.6°</td>
</tr>
<tr>
<td>2</td>
<td>2.1</td>
<td>0.055</td>
<td>+ 21.6°</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>0.055</td>
<td>+ 5.1°</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>0.056</td>
<td>+ 1.8°</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>0.072</td>
<td>- 0.1°</td>
</tr>
<tr>
<td>3</td>
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<td>0.083</td>
<td>+ 29.1°</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>0.045</td>
<td>+ 15.0°</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>0.057</td>
<td>+ 8.1°</td>
</tr>
<tr>
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<td>+ 40.8°</td>
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<td>+ 25.9°</td>
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<tr>
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<td>0.063</td>
<td>+ 47.1°</td>
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<td>0.056</td>
<td>+ 40.4°</td>
</tr>
<tr>
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<td>0.032</td>
<td>+ 34.0°</td>
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<td>+ 48.1°</td>
</tr>
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<td>+ 48.7°</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>0.024</td>
<td>+ 48.3°</td>
</tr>
</tbody>
</table>

\(^a\) Initial molecular weight \(\bar{M}_n = 860\).

\(^b\) The packing material consisted of 7 g of polymer coated on 20 g of porous glass beads.

\(^c\) The initial \([\alpha]_D^28\) in CHCl\(_3\) of each run is 1: 0°; 2: +6.5°; 3: +19.3°; 4: +28.1°; 5: +41.5°; 6: +47.5°.

\(^d\) In every experiment the weights of the supported and the eluted polymer differed by no more than 5%.

\(^e\) In chloroform. \(c 0.25-2.0\).

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 \([\alpha]_D^28 = +48°\) 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 \([\alpha]_D^28 = +56°\) (estimated error 2°), while the third fraction (± 20 weight %) has \([\alpha]_D^28 = +26°\). Molecular weight measurements reveal that the specific rotation increases with molecular weight until the maximum of \([\alpha]_D^28 = +56°\) 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 \((\text{CH}_3)_2\text{C}-\text{N-C=}[\text{M}]_D^28 = 46°\). In SI units \([\alpha]_D^2(\text{CHCl}_3, 293 \text{ K}, 578 \text{ nm}) = 56°\) should be \(\alpha_n\) \((\text{CHCl}_3, 293 \text{ K}, 578 \text{ nm}) = 9.8 \times 10^{-3} \text{ m}^2\text{kg}^{-1}\). The rotation does not decrease when the compound is kept in solution at room temperature for months.

We also observed an increase in \([\alpha]\) with increasing molecular weight for poly(\(\text{S}\)-3-phenethyliminomethylene): a sample of \(\bar{M}_n = 1830\) had \([\alpha]_D^28\) of \(-250°\) while samples of \(\bar{M}_n = 14,000\) and 66,001 had \([\alpha]_D^28\) of \(-350°\) (see also ref. 7). The corresponding low molecular weight model, \(\text{CH}_3\text{CH(Ph)-N=C(C)}_3\text{H}_3\) has \([\alpha]_D^28 = -90°\) (cf. ref. 12.). These observations of increasing \([\alpha]\) with increasing molecular weight are in line with calculations\(^13\) 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(\(\text{tert}-\text{butyl})-\) with poly(\(\text{sec}-\text{butyliminomethylene}\)) are probably more important than interactions with the chiral side chain of the supporting polymer. It supports our suggestion\(^8\) that the sec-butyl isocyanide has polymerised stereoselectively (cf. Pino et al.\(^14\)).


\(^11\) Calculated from a Mark-Houwink equation, given in Ref. 5.

\(^12\) H. E. Smith, M. E. Warren and A. W. Ingersoll, J. Am. Chem. Soc. 84, 1513 (1962).


Poly(tert-butylaminomethylene). N-tert-Butylformamidom was made according to a literature method and converted into the isocyanide by the method of Casanova at but 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 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 (C=N); this shoulder can be assigned to low temperature amide bands.

The polymer was isolated as a white powder in a yield of 30%. IR (KBr): 1641 cm⁻¹ (C=N); the IR spectrum 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 glass filter, washed with 25% aqueous methanol and dried in a vacuum. The supernatant liquid was decanted and an additional amount of 70 ml of methanol 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.

The corresponding optically active formamides were prepared heterogeneously by 1.5 mol % anhydrous nickel chloride. The specific optical rotations of the samples were: \( [\alpha]_D^{20} +7.44° \) (neat); \( [\alpha]_D^{20} +17.9° \) (c 0.1, CHCl₃) \( [\alpha]_D^{20} +15.8° \) (c 15.9, CHCl₃). The isocyanide was prepared as described for tert-butyl isocyanide. Yield 95% \( [\alpha]_D^{20} +14.2° \) (neat, \( d^2 0.766 \text{ g/ml} \); \( [\alpha]_D^{20} +47.0° \) (c 1.8, chloroform) \( [\alpha]_D^{20} +48.9° \) (c 12.4, chloroform).

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 NiCl₂·6H₂O 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 (-) -sec-butylicyanide 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.

The formamides were converted into the optically active isocyanides by reaction with 10% excess of ethyl formate 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 \( \approx 40 \text{ ml} \). This solution was added dropwise to a vigorously stirred mixture of 500 ml of methanol and 150 ml of water. The flocky yellow precipitate was collected on a glass filter, washed with 25% aqueous methanol and dried in a vacuum. The yield was 90%; \( [\alpha]_D^{20} +0.70 \text{ dl/g (toluene, 30.00°C)} \); \( [\alpha]_D^{20} = -178° \) (c 4.25, 96% ethanol).

The formamides were converted into the optically active isocyanides by the method of Appel. For both enantiomers the yield was approximately 50%. \( [\alpha]_D^{10} = +17.9° \) (c 0.1, CHCl₃), \( [\alpha]_D^{20} = -250° \) (c 0.1, CHCl₃) and \( [\alpha]_D^{20} = -250° \) (c 0.1, CHCl₃). The samples various had similar spectroscopic properties; see Ref. 25.

Poly(3-sec-butylicyanomethylene), coated on porous glass

(S)-(-) -sec-butylicyanide. sec-butylicyanide was resolved through fractional crystallisation of the bitartrate from water, according to the literature. The free amine was liberated with an excess of 50% aqueous sodium hydroxide and distilled from powdered potassium hydroxide. (S)-Enantiomer \( [\alpha]_D^{20} +8.28° \) (neat); \( [\alpha]_D^{20} +8.10° \) (neat, \( d^2 0.766 \text{ g/ml} \); \( [\alpha]_D^{20} +7.44° \) (neat)).

This amine was converted in almost quantitative yield into the N-sec-butylicyanomethylene by treatment with 10% excess ethyl formate; \( [\alpha]_D^{20} = +17.9° \) (c 4.9, CHCl₃) \( [\alpha]_D^{20} = +15.8° \) (c 15.9, CHCl₃). The isocyanide was prepared as described for tert-Butyl isocyanide. Yield 95% \( [\alpha]_D^{20} +44.7° \) (neat, \( d^2 0.766 \text{ g/ml} \); \( [\alpha]_D^{20} +47.0° \) (c 1.8, chloroform) \( [\alpha]_D^{20} +48.9° \) (c 12.4, chloroform).

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