

Figure 1. The molecular structure of $[\text{Me}_2\text{GeRe}(\text{CO})_4\text{C}(\text{O})\text{Me}]_2$.¹⁰ Selected bond lengths (Å) are: Re-Ge = 2.591(3); Ge-O5' = 1.96(2); C5-O5 = 1.27(3); Re-C5 = 2.14(3); av Re-C(1-4) = 1.92(3); av C(1-4)-O(1-4) = 1.15 (3). Selected bond angles (deg) are: Re-C5-C8 = 111 (2); Re-C5-O5 = 121 (2); C8-C5-O5 = 128 (2); Ge-O5'-C5' = 139 (2); Ge-Re-C5 = 82.8 (6); Re-Ge-O5' = 107.6 (4).

-25° , thermodynamic parameters for this process were determined to be $\Delta H^\circ = 6.7 \pm 0.3$ kcal and $\Delta S^\circ = 27.9 \pm 1.4$ eu.³

The ^{13}C nmr spectrum in CDCl_3 at -30° confirmed the presence of two distinct species in solution. Particularly noteworthy were two peaks at -337.72 and -335.20 ppm, relative to TMS, which established that both species contained carbene carbon atoms.⁴

It has not been possible to obtain crystals of **1** suitable for crystallographic study. We therefore prepared the rhenium analog⁵ of **1** and have been able to obtain satisfactory crystals of it despite its lesser stability in solution.⁶

The X-ray diffraction study showed that the crystals contained the dimer rather than the monomer.⁷ The crystals exhibited twinning and the apparent space group and unit cell were determined to be $I2/m$, $a = 9.639(8)$ Å, $b = 11.504(9)$ Å, $c = 11.140(9)$ Å, and $\beta = 97.22(1)^\circ$. This cell is a composite of two orientations of a triclinic cell with space group $P\bar{1}$ and approximate dimensions $a \approx b = 9.05$ Å, $c = 9.63$ Å, $\alpha = 106.9^\circ$, $\beta = 118.0^\circ$, and $\gamma = 101.0^\circ$. The density was measured by flotation as $2.37(2)$ g cm^{-3} and is in reasonable agreement with the calculated value 2.40 g cm^{-3} (assuming a molecular weight of 887.7 and two molecules in the $I2/m$ cell). Intensity data were collected on an automatic Picker four-circle diffractometer within the angular limits $0 < 2\theta \leq 45^\circ$, $0 \leq \phi < 360^\circ$, $-90^\circ \leq \chi \leq 90^\circ$ using Mo $K\alpha$ radiation. The data

(3) At the concentration used in the variable temperature study (52.8 mg ml^{-1}), the dimer peak above -25° was of low and not easily measurable intensity and decreased to zero before ambient temperature was reached. This was not a process of peak coalescence. Furthermore, dimer would not be detected at dilutions normally used in infrared spectroscopy.

(4) G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Waller, and L. J. Todd, *Inorg. Chem.*, **12**, 1071 (1973).

(5) This complex has been characterized by analysis and spectroscopy.

(6) Crystals were grown by vigorously bubbling nitrogen through a dichloromethane-*n*-heptane solution to the point of turbidity, followed by cooling to -15° .

(7) The mass spectrum of this dimeric species shows only peaks due to the monomeric form. On this basis, the mass spectra of **1** and its diphenyl analog,¹ which also show only monomer, would be consistent with a dimeric solid form for these compounds although a monomeric solid cannot be ruled out.

were corrected for absorption effects ($\mu = 130$ cm^{-1}) and merged to give 692 significant observations.

The structure was solved and refined by conventional methods and has refined to an R factor of 0.039.⁸ The symmetry of the dimer is C_2 but the twinning introduces a mirror plane and the composite of the two interpenetrating images (each of occupancy 0.5) has symmetry C_{2h} and is consistent with two molecules in the apparent $I2/m$ cell. The twinning appears to be similar to that described for $\text{Co}_4(\text{CO})_{12}$.⁹ The electron density peaks due to the different half-weight images were well resolved in the important central region and assignment of bonds (*i.e.*, image separation) was straightforward once the dimeric nature of the molecule was recognized.

The molecular structure of $[\text{Me}_2\text{GeRe}(\text{CO})_4\text{C}(\text{O})\text{Me}]_2$ is shown in Figure 1.¹⁰ The molecule contains an unusual eight-membered, heterocyclic ring of rhenium, germanium, oxygen, and carbon atoms. Selected bond lengths and angles are given in the caption to Figure 1. Of particular interest are the planarity of the carbene carbon atoms and the three attached groups and the rather long germanium-oxygen distance, which may result from the strong interaction between the oxygen and carbene carbon.

The structure provides excellent support for the dimer-monomer equilibrium described above, as well as suggesting that the four-membered heterocyclic structure earlier proposed¹ for the monomeric form of **1** is correct.

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Supplementary Material Available. A listing of atom coordinates of $[\text{Me}_2\text{GeRe}(\text{CO})_4\text{C}(\text{O})\text{Me}]_2$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105×148 mm, $24\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-5931.

(8) Refinement was carried out in $I2/m$. The space group $P\bar{1}$ was also used varying the relative weights of the two components but essentially refined to equal weights, which is the $I2/m$ solution.

(9) C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969).

(10) See paragraph at end of paper regarding microfilm material.

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Chirality in Polyisocyanides

Sir:

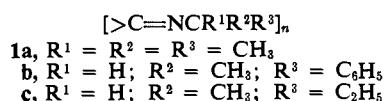
It has been suggested¹⁻³ from Stuart models that the backbone of polyisocyanides (**1**) has the conformation of a tightly coiled helix. In particular this would be

(1) (a) R. J. M. Nolte, R. W. Stephany, and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **92**, 83 (1973); (b) R. J. M. Nolte, Ph.D. Thesis, University of Utrecht, 1973.

(2) F. Millich and R. G. Sinclair, *J. Polym. Sci., Part C*, **22**, 33 (1968).

(3) F. Millich and G. K. Baker, *Macromolecules*, **2**, 122 (1969).

the case for polymers of isocyanides with bulky side groups like **1a**.



If the models are realistic, polyisocyanides consist of racemic mixtures of left-handed and right-handed helices. In order to prove the occurrence of enantiomers, we first tried to synthesize the polymers asymmetrically. Polymerization of isocyanides was performed in benzene solution at 25° by nickel chloride and nickel acetylacetonate in the presence of (–)-borneol. The polymers obtained did not show optical activity. The same negative result was found when the polymerization was carried out in (+)-*sec*-butyl alcohol as a chiral solvent.

However, a slightly asymmetric reaction was observed when racemic α -phenylethyl isocyanide was polymerized in methanol at 25° with (+)-nickel alaninate as a chiral catalyst. The polymer (**1b**) isolated at different intervals showed a weak negative optical rotation, $[\alpha]_{578}^{27} -0.4^\circ$ (*c* 2, benzene). The observed optical activity does not arise from the catalyst which has an opposite sign of rotation. Nevertheless, no definite conclusions can be drawn from this small effect with regard to the secondary structure of polyisocyanides. Moreover, an optical rotation found in **1b** is not of necessity connected with helix conformations, because the monomeric isocyanide is a racemic mixture of enantiomers which might give some asymmetric selective polymerization with a chiral catalyst.

A resolution of polyisocyanides by column chromatography on a chiral support appeared to be successful. As supporting materials poly[(+)-*sec*-butyl isocyanide] and poly[(–)-*sec*-butyl isocyanide], (+)-**1c** and (–)-**1c**, were used. These polymers were synthesized from the corresponding optically active monomers⁴ (optical purity 96%) by 0.1 mol % nickel chloride in methanol at 25°. These polymers **1c** are highly insoluble in organic solvents and water; their optical rotation could not be measured.

With (+)-**1c** as a supporting polymer a partial resolution has been obtained of poly(*tert*-butyl isocyanide) (**1a**), which is soluble in chloroform. A typical example is given in Table I. Reversed signs were ob-

Table I. Chromatographic Resolution^a of Poly(*tert*-butyl isocyanide). Supporting Medium Poly[(+)-*sec*-butyl isocyanide]^b

Fraction	Fraction weight/g	$[\alpha]_{578}^{20}$ ^c
1	0.094	+5.2°
2	0.066	0.0°
3	0.061	–1.9°
4	0.066	–5.5°

^a Eluent chloroform, at 25°. ^b Weight of supporting polymer 7 g, weight of supported polymer 0.300 g, total polymer eluted 0.287 g. ^c In chloroform.

served when (–)-**1c** was used as supporting material. The highest specific optical rotation measured so far for fractions of **1a** is $[\alpha]_{578}^{20} -16^\circ$. This result was

(4) Details will be published in a full paper; we wish to thank Mr. Th. G. Aerts for experimental assistance and Mr. F. X. R. van Leeuwen for recording the ORD spectrum.

obtained after chromatographing a sample of **1a** three times over (+)-**1c**. ORD⁴ shows a gradual increase of rotation from 600 to 400 nm by a factor of 6.

Attempts to resolve low molecular weight compounds such as *sec*-butylamine and *sec*-butyl alcohol by chromatographing over the same supporting material have failed. This suggests that the conformation of the principal chain of the polymers plays an important role in the resolution process of **1a**.⁵

Reports of polymer resolution are scarce.⁶ Pino, *et al.*,⁵ described the resolution of racemic poly(4-methyl-1-hexene), which has chiral atoms in the lateral chain, by using an optically active poly(*S*-3-methyl-1-pentene) as chromatographic support. As far as we are aware, resolution of polymers, which have chiral centers neither in the principal nor in the lateral chain, has not been reported before.

(5) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Natta, *J. Amer. Chem. Soc.*, **84**, 1487 (1962).

(6) (a) R. C. Schulz and E. Kaiser, *Advan. Polym. Sci.*, **4**, 236 (1965); (b) T. Tsuruta, *J. Polym. Sci., Part D*, **6**, 179 (1972).

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Photoisomerization of 2-Pyridylacetonitrile to Anthranilonitrile

Sir:

During the course of our investigations of the photochemical behavior of α -alkylpyridines substituted at the side-chain,¹ 2-pyridylacetonitrile (**1**) was found to photoisomerize to anthranilonitrile (**2**) in a good yield. The reaction does not occur in the absence of ultraviolet light.

Preparative-scale photolysis² of **1** (3.4×10^{-2} M) in ethyl ether–*tert*-butyl alcohol, followed by separation by column chromatography (Florisil) led to the isolation of **2** (mp 47–48°) in a yield of 44.3%. The mass spectrum of the photoproduct (M^+ 118) indicates that this is an isomer of **1**. The infrared spectra of the product showed strong bands at 1620, 3350, and 3450 cm^{-1} , suggestive of the aromatic primary amine. The structure of the product was established by comparison with the spectral properties of an authentic sample.^{4,5} Irradiation of **1** in other solvents also afforded **2** in various yields.⁶

(1) K. Takagi and Y. Ogata, The annual meeting of the Chemical Society of Japan, April 1974, Osaka, Japan, Abstract III, 1611.

(2) 2-Pyridylacetonitrile (**1**) was prepared by dehydration of 2-pyridylacetamide³; nmr (CCl_4) δ 8.42 (m, 1 H), 7.43 (m, 3 H), 3.84 (s, 2 H); $\lambda_{\text{max}}^{\text{MeOH}}$ 266 nm (ϵ 1900), 260 (ϵ 2600), 255 (ϵ 2300). Preparative-scale photolyses were carried out under nitrogen at 20–25° for 15 hr using an internal water-cooled mercury arc lamp (Halos HIP 300-W).

(3) N. Sperber, D. Papa, E. Schwenk, M. Sherlock, and R. Fricano, *J. Amer. Chem. Soc.*, **73**, 5752 (1951).

(4) J. Pinnow and C. Sämman, *Ber.*, **29**, 624 (1896).

(5) **2**: $\lambda_{\text{max}}^{\text{MeOH}}$ 247 nm (ϵ 6600), 324 (ϵ 3800); ir (KBr) (cm^{-1}) 3450, 3350, 2200, 1620, 745; nmr (CCl_4) δ 7.3–7.4 (m, 4 H), 4.5 (s, 2 H, exchangeable with D_2O).

(6) In the solvents shown in Table I, **2** is the major photoproduct accompanied by a trace of some other components by glc analysis (PEG 20M on Chamelite CS, 2 m at 100–250°). In some cases, an appreciable amount of polymeric material was obtained. In alcohols bearing an α -hydrogen, e.g., ethanol, another photoproduct was obtained which is probably a 1:1 adduct of **1** with the alcohol.^{1,7}

(7) T. J. van Bergen and R. M. Kellogg, *J. Amer. Chem. Soc.*, **94**, 8451 (1972), and references therein.